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**(54) Polymer for hair-care products**

Polymer für Haarpflegemittel

Polymères pour des produits de traitement des cheveux

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**Description**

The present invention relates to novel polymers suitable for use in hair-care products. More particularly, the present invention relates to a polymer comprising as an essential constituent units of a hydrophilic unsaturated monomer which affords hair an excellent brilliance and gloss and a smooth feeling and has an excellent washability, and into which a polysiloxane group has been introduced.

The polymers in accordance with the present invention can be used for providing hair with settability, softness, gloss, smooth feeling, smooth combing, recovery from damages, manageability and the like.

In hair-care products such as a shampoo, a rinse, a hair treatment product, a hair setting product or a cold permanent wave solution have heretofore been used oily components such as silicone compounds, ester compounds, hydrocarbon compounds or the like in an emulsified, solubilized or dissolved state, for the purpose of providing hair with brilliance, gloss and smoothness. The silicone type compounds among them have these years been used extensively because of their excellent properties.

Specific examples of application of silicone compounds include (i) hair-care products into which silicone oils such as polydimethylsiloxane, polymethylphenylsiloxane or the like and their emulsion have been incorporated; (ii) aerosol foam type hair setting products such that an etherified silicone such as a polydimethylsiloxane-polyoxyalkylene block copolymer or the like has been incorporated into a hair-fixative polymer such as a cationic polymer or an amphoteric polymer to form, together with a propellant, the aerosol products (Japanese Patent Laid-Open Publication No. 135319/88); (iii) shampoos and rinses into which an aminated organopolysiloxane emulsion has been incorporated (Japanese Patent Laid-Open Publication No. 307811/63); (iv) hair conditioning product and hair-setting products such that an aminated organopolysiloxane emulsion has been incorporated into a cationic polymer compound and an amphoteric polymer compound, respectively, to form the hair conditioning product and hair-setting products (Japanese Patent Laid-Open Publication No. 275515/88); and (v) hair-care products in which polydimethylsiloxane or polymethylphenylsiloxane having a high molecular weight is used (Japanese Patent Laid-Open Publication No. 243019/88).

However, the silicone oils or the etherified silicones when used may cause problems such as giving sticky feeling to hair or undergoing reverse transition of silicone from hair to hand or clothing if they are formulated in a large amount or if the product is used repeatedly for a long time. Emulsions of silicones may have problems in dispersion stability. Silicones having a high molecular weight may have problems in the compatibility with hair care resins or additives, so that they have restrictions in formulation whereby their applicability in a variety of hair-care products is restricted.

The silicone compounds having no such hydrophilic groups as a polyether group are difficult to be removed by usual hair washing, and thus when consumers use the products into which the less hydrophilic silicone compounds have been formulated for a long period repeatedly, hair tends to be hydrophobic and causes problems in hair dyeing or permanent waving.

The object of the present invention is to solve the aforementioned problems and to provide a polymer for hair-care products which provides hair with an excellent gloss and brilliance and a smooth feeling without stickiness and will not be accumulated in the hair and cause no problems for being formulated into cosmetics.

The invention provides use in a hair-care product of a copolymer comprising (a) a unit of a hydrophilic ethylenically unsaturated monomer in a quantity of 15 to 99.9% by weight; (b) a unit of an ethylenically unsaturated monomer having a polysiloxane group in a quantity of 0.1 to 85% by weight; and (c) a unit of a hydrophobic ethylenically unsaturated monomer in a quantity of 0 to 84.9% by weight. In a hair care product comprising said copolymer, the copolymer is dissolved in water and/or alcohol in a concentration of 0.5 to 10 % by weight.

In the present invention, an ethylenically unsaturated monomer having a polysiloxane group (b) is copolymerized with a hydrophilic ethylenically unsaturated monomer (a) and, if necessary, with a hydrophobic ethylenically unsaturated monomer (c), so that the defects in conventional silicone compounds such as generation of the sticky feeling of hair or the reverse transition of silicone encountered when the silicone compounds are formulated in a large quantity or on the use for a long period repeatedly can be solved thanks primarily to the use of the compound (b), and the silicone can be easily removed by washing hair thanks primarily to the component (a). Further, a hydrophilic ethylenically unsaturated monomer component (a) and a hydrophobic ethylenically unsaturated monomer component (c) are appropriately chosen in terms of their types and relative proportions, so that the polymer can now be incorporated into hair care products without restriction.

**DESCRIPTION OF THE PREFERRED EMBODIMENT OF THE INVENTION****[I] Polymer****Unsaturated Monomer**

The polymer suitable for use in the present invention is obtained by copolymerizing two essential monomers,

namely (a) a hydrophilic unsaturated monomer and (b) an unsaturated monomer having a polysiloxane group, and an optional monomer, namely (c) hydrophobic unsaturated monomer. Each of these monomers of the categories (a), (b) and (c) can be used in admixture within respective categories.

#### Hydrophilic unsaturated monomers (a):

Preferably, the hydrophilic unsaturated monomers as the component (a) are hydrophilic unsaturated monomers of a cationic, anionic, nonionic or amphoteric nature and polymerizable through radical polymerization mechanism. It is preferable that they have a solubility in water in a range of 10 g/100 g of water or more (25°C).

Examples of the cationic unsaturated monomers include

(i) monomers derived from acrylic acid or methacrylic acid, which is referred to hereinafter collectively as (meth)acrylic acid, and a quaternized epihalohydrin product of a trialkylamine having 1 to 4 carbon atoms in the alkyl such as (meth)acryloyloxyhydroxypropyltrimethylammonium chloride and (meth)acryloyloxyhydroxypropyltriethylammonium bromide;

(ii) amine derivatives of (meth)acrylic acid or amine derivatives of (meth)acrylamide derived from (meth)acrylic acid or (meth)acrylamide and a dialkylalkanolamine having C<sub>1</sub> to C<sub>4</sub> alkyl groups such as dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, or dimethylaminopropyl (meth)acrylamide; and

(iii) derivatives of the products of the group (ii) above by (1) neutralization with an acid such as hydrochloric acid, or lactic acid, (2) denaturation with a halogenated alkyl such as methyl chloride, ethyl chloride, methyl bromide, or ethyl iodide, (3) denaturation with a halogenated fatty acid ester such as ethyl monochloroacetate, or methyl monochloropropionate, and (4) denaturation with a dialkyl sulfate such as dimethyl sulfate, or diethyl sulfate.

Furthermore, the cationic unsaturated monomers include amine derivatives of allyl compounds such as diallyldimethylammonium chloride and the like.

These cationic unsaturated monomers can be copolymerized in the form as such, or as an alternative they can be copolymerized in the form of their precursors, which are then cationized by a so-called cationizing agent. More particularly, dimethylaminoethyl (meth)acrylate is copolymerized, and the copolymer obtained will then be cationized by a quaternizing agent such as hydrochloric acid, ethyl monochloroacetate, dimethyl sulfate to form a desired copolymer of the cationic unsaturated monomer.

Examples of the anionic unsaturated monomers include:

(i) unsaturated carboxylic acid monomers such as (meth)acrylic acid, maleic acid, maleic anhydride, itaconic acid, fumaric acid, and crotonic acid;

(ii) half esters of an unsaturated polybasic acid anhydride such as succinic anhydride, phthalic anhydride with a hydroxyl group-containing (meth)acrylates such as hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate,

(iii) monomers having a sulfonic acid group such as styrenesulfonic acid, sulfoethyl (meth)acrylate, and

(iv) monomers having a phosphoric acid group such as acid phosphoxyethyl (meth)acrylate, 3-chloro-2-acid phosphoxypropyl (meth)acrylate.

These anionic unsaturated monomers can be used in the form of an acid or after partial or complete neutralization, or they can be copolymerized in the form of acid and then neutralized partially or completely. Examples of the bases used for neutralization include alkali metal hydroxides such as lithium hydroxide, potassium hydroxide, sodium hydroxide, aqueous ammonia, amine compounds such as mono-, di- or triethanolamine, triethylamine, morpholine, aminomethylpropanol, aminoethylpropanediol.

Examples of the nonionic unsaturated monomers include monomers derived from (meth)acrylic acid or (meth)acrylamide and an alkylene oxide having 2 to 4 carbon atoms such as hydroxyethyl (meth)acrylate, polyethyleneglycol mono(meth)acrylate, methoxypolyethyleneglycol mono(meth)acrylate, methoxypoly(ethylene glycol/propylene glycol) mono(meth)acrylate, polyethylene glycol di(meth)acrylate, N-polyalkylenoxy(meth)acrylamide; acrylamide, N-vinylpyrrolidone.

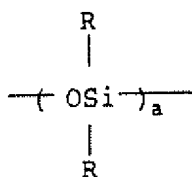
Examples of the amphoteric monomers include zwitter ionized derivatives of the aforementioned amine derivatives of (meth)acrylic acids or the amine derivatives of (meth)acrylamide such as dimethylaminoethyl (meth)acrylate, dimethylaminopropyl(meth)acrylamide by a halogenated fatty acid salt such as potassium monochloroacetate, sodium monobromopropionate, aminomethylpropanol salt of monochloroacetic acid, triethanolamine salt of monochloroacetic acid; and modified products with propanesultone of the aforementioned amine derivatives of (meth)acrylic acid or (meth)acrylamide.

These amphoteric unsaturated monomers, like the aforementioned cationic unsaturated monomers, can be copoly-

lymerized in the form as such or as an alternative they can also be copolymerized in the form of their precursors, which are then converted into amphoteric state. It is also possible to remove the salt produced as a by-product of amphotericization by filtration or ion-exchange, if necessary, before copolymerization step or after the copolymerization-amphotericization step. These technologies is described in detail in Japanese Patent Laid-Open Publication No. 92809/B1.

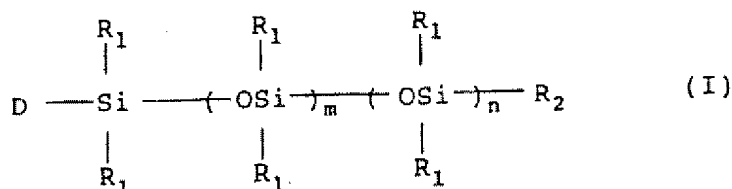
The hydrophilic unsaturated monomer is used in an amount of 15 to 99.9% by weight per weight of total monomers. If the amount is less than 15% by weight, the copolymer thus obtained has problems that it is hardly soluble in water and/or an ethanolic solvent or it is difficult to be removed upon hair washing. The amount of the monomer can be selected at will according to the uses with the upper limit of 99.9% by weight. In other words, the hydrophilic unsaturated monomer is preferably used in an amount of 15 to 59.5% by weight when the polymer is used as a hair-setting polymer and 30 to 99.5% by weight when the polymer is used as a hair-conditioning polymer. Polysiloxane group containing unsaturated monomer (b):

The polysiloxane group-containing unsaturated monomer as the component (b) is a monomer which has at least one unsaturated group having radical polymerizability and a polysiloxane group



wherein  $a = 1$  to 150.

Specifically, compounds represented by the following formula (I) are mentioned:



wherein D,  $\text{R}_1$ ,  $\text{R}_2$ , m and n have the following meanings, respectively:

D = an unsaturated group having radical polymerizability such as a vinyl group, a vinylalkylene group, a vinylhydroxyalkylene group, an acryloyloxyalkylene group, a methacryloyloxyalkylene groups, an acryloyloxyhydroxyalkylene group and a methacryloyloxyhydroxyalkylene group;

$\text{R}_1$  = a hydrogen atom, a phenyl group, an alkyl group having 1 to 10 carbon atoms, a polyoxyalkylene group, a polyoxyalkylene group of which end has been substituted by an ether or ester group, a polyalkylenepolyamine group, a fatty acid group or a polysiloxane group, respectively;

$\text{R}_2$  = a hydrogen atom, a phenyl group, an alkyl group having 1 to 10 carbon atoms, a polyoxyalkylene group, a polyoxyalkylene group of which end has been substituted by an ether or ester group, a polyalkylenepolyamine group, a fatty acid group or a polysiloxane group, or an unsaturated group having radical polymerizability such as a vinyl group, a vinylalkylene group, a vinylhydroxyalkylene group, an acryloyloxyalkylene group or a methacryloyloxyalkylene group;

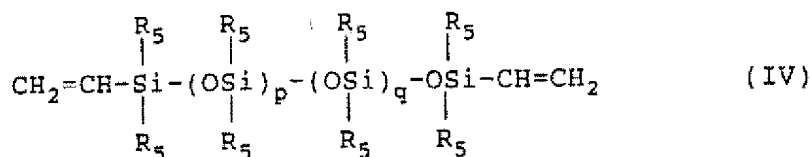
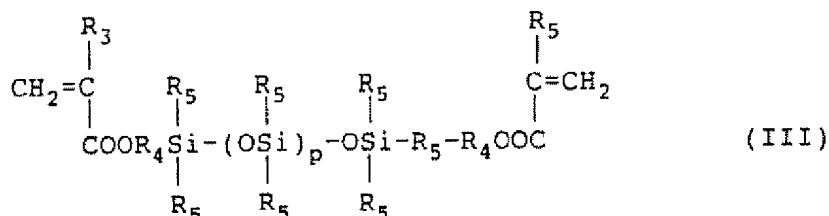
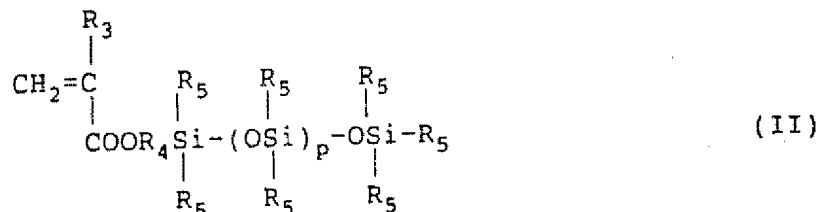
m = an integer from 4 to 150; and

n = an integer from 0 to 150, wherein the sum of m and n is within 150.

In the above-described formula (I), the sum of m and n is preferably in the range of 4 to 150. If the sum is less than 4, the polymer obtained by the copolymerization cannot exhibit the advantages inherent in the silicone compound. If the sum exceeds 150, the copolymerizability with the unsaturated monomers of the components (a) and (b) is undesirably lowered.

Embodiments of the unsaturated monomer having a polysiloxane group include the unsaturated monomers illustrated by the following formulae (II) - (IV):





wherein  $\text{R}_3$  -  $\text{R}_5$ ,  $p$  and  $q$  have the following meanings independently of each other between the formulae:

$\text{R}_3$  = a hydrogen atom or a methyl group;

$\text{R}_4$  = an alkylene group having 1 to 4 carbon atoms;

$\text{R}_5$  = an alkyl group having 1 to 10 carbon atoms or a phenyl group;

$p$  = an integer of 1 or more; and

$q$  = an integer of 1 or more, wherein the sum of  $p$  and  $q$  are within 150.

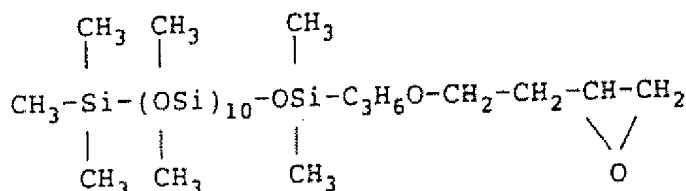
The unsaturated monomers illustrated by the general formula (II) can be obtained as commercially available products (manufactured by Chisso Corporation) such as FM0711 (trade name;  $p = 10$ ,  $\text{R}_3$  = a methyl group,  $\text{R}_4$  = a propylene group, and  $\text{R}_5$  = a methyl group in the aforementioned formula (II); referred to as polysiloxane FM0711 in the preparation example below), FM0721 ( $p = 60$ ,  $\text{R}_3$  = a methyl group,  $\text{R}_4$  = a propylene group, and  $\text{R}_5$  = a methyl group in the aforementioned formula (II); referred to as polysiloxane FM0721 in the preparation example below) and FM0725 ( $p = 130$ ,  $\text{R}_3$  = a methyl group,  $\text{R}_4$  = a propylene group, and  $\text{R}_5$  = a methyl group in the aforementioned formula (II); referred to as polysiloxane FM0725 in the preparation example below).

The monomers illustrated by the general formula (III) can be easily obtained by the reaction of a polysiloxane having both ends of silanol and a (meth)acryloyloxyalkylene (having 1 to 4 carbon atoms) di(alkyl (having 1 to 4 carbon atoms) or phenyl) halosilane.

The unsaturated monomers illustrated by the general formula (IV) can be obtained as commercially available products (manufactured by Chisso Corporation) such as FP2231 (trade name;  $p = 30$ ,  $q = 5$ ,  $\text{R}_5$  = a methyl group and  $\text{R}_6$  = a phenyl group; referred to as polysiloxane FP2231 in the preparation example below), FP2241 and FP2242.

The polysiloxane group-containing unsaturated monomers illustrated by the general formulae (II) - (IV) can be copolymerized in the form as such. Alternatively, they can be copolymerized in the form of their precursor and a polysiloxane group will then be added. Specifically, a polysiloxane group can be introduced by copolymerizing the monomer in the form of (meth)acrylic acid and then reacting with a polysiloxane having a terminal epoxy group (for example, a compound illustrated by the following structural formula (1), this compound being referred to as polysiloxane FM0521 in the preparation example below). A polysiloxane group can also be introduced by polymerizing the monomer in the form of (meth)acryloyloxyalkylenedialkylchlorosilane and then reacting with a polysiloxane having a terminal epoxy group or a polysiloxane having a terminal modified with an amino group.

Structural formula (1):



The quantity of copolymerization of the polysiloxane group containing unsaturated monomer (b) is in the range of 0.1 to 85% by weight, preferably 0.5 to 70% by weight, more preferably 0.5 to 20% by weight, of the total monomer weight. If the amount is less than 0.1% by weight, the copolymer obtained cannot afford hair an excellent gloss and brilliance or a smooth feeling. If the amount of the monomer exceeds 85% by weight, it will cause problems when it is incorporated into cosmetics or when it is used repeatedly over a long period.

If the monomer represented by the formula (I) described above is monofunctional and the sum of m and n is 80 or more, the copolymerizability of the monomer decreases, so that it is effective to use a bifunctional monomer wherein R<sub>2</sub> is a vinyl group, an acryloyloxy group or a methacryloyloxy group in combination with the monofunctional monomer.

## Hydrophobic unsaturated monomer (c):

The hydrophobic unsaturated monomer of the component (c) is a hydrophobic unsaturated monomer having radical polymerizability which is used, if necessary, in order to afford the copolymer obtained a hydrophobic property and the strength, hardness and softness of film derived therefrom. The hydrophobic unsaturated monomer has preferably a solubility in water in the range of less than 10 g/100 g in water (25°C).

Examples of the hydrophobic unsaturated monomers include, for example, (a) saturated and unsaturated alkyl (meth)acrylates having 1 to 24 carbon atoms in the alkyl such as methyl (meth)acrylate, allyl (meth)acrylate, isobutyl (meth)acrylate, cyclohexyl (meth)acrylate, octyl (meth)acrylate, lauryl (meth)acrylate, oleyl (meth)acrylate, behenyl (meth)acrylate; (b) hydrophobic (meth)acrylates and their derivatives such as butoxyethyl (meth)acrylate, benzyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, ethyleneglycol di(meth)acrylate, 1,3-butyleneglycol di(meth)acrylate, diacetoneacrylamide; (c) aromatic unsaturated monomers such as styrene, chlorostyrene, vinyltoluene; and (d) vinyl esters such as vinyl acetate.

The amount of the hydrophobic unsaturated monomer polymerized is in the range of 0 to 84.9% by weight to the total monomer weight, and this monomer is not an essential component. If the amount of this monomer exceeds 84.9% by weight, the copolymer thus obtained may have problems that it becomes hardly soluble in water and/or an ethanolic solvent or it is difficult to be removed from hair upon hair washing. The amount of the monomer can be selected at will according to the uses with the upper limit of 84.9% by weight. The hydrophobic unsaturated monomer is preferably used in an amount of 40 to 84.5% by weight when the polymer is used as a hair-setting polymer and 0 to 69.5% by weight when the polymer is used as a hair-conditioning polymer.

When a bifunctional unsaturated monomer such as ethyleneglycol di(meth)acrylate, allyl (meth)acrylate is used, it is preferably used in an amount of 2% by weight or less to the total monomer weight.

### Formation of copolymer

The unsaturated monomers can be copolymerized by well-known radical polymerization methods such as bulk polymerization, solution polymerization, suspension polymerization, emulsion polymerization.

Preferred polymerization method is a solution polymerization method, which is conducted by a process comprising dissolving monomers in a solvent, adding a polymerization initiator and stirring under heating the mixture under the nitrogen stream.

the solvent is preferably water and an alcohol such as methanol, ethanol, isopropanol, ethyleneglycol and butylcellosolve. These solvents can be used in combination. The polymerization initiator is preferably a peroxide such as benzoyl peroxide, lauroyl peroxide and an azo compound such as azobisisobutyronitrile or the like.

The monomers concerned are usually used in such a way that all of them in types and amounts are added to the polymerization at once from the initiation of polymerization, but alternatively they can be used in such a way that some of them in types and/or amounts are added to polymerization separately. The solvent is preferably used in such an amount that the copolymer solution obtained has a polymer concentration of 10 to 65% by weight. The amount of the monomers charged may be determined in consideration of factors such as the copolymerizability or the conversion so that the copolymer obtained has a predetermined composition. It goes without saying that the monomers charged has the same composition as that of the copolymer in the case of the conversion of 100%.

The molecular weight of the copolymer can be decided at will by appropriately selecting the polymerization conditions such as polymerization temperature, the kinds and amounts of polymerization initiators, addition methods, the amounts of solvent used, the chain transfer agents when used. In general, the copolymers obtained have preferably the molecular weight in the range of 1,000 to 500,000.

The copolymer can be obtained as a solid by removing the solvent from a copolymer solution, or the solid thus obtained can be diluted with any solvents to obtain a copolymer solution, which are used for further applications. The copolymers thus obtained and the solutions may be used in admixture of the two or more.

### (II) Use of the polymer/hair-care products

The copolymer thus obtained is preferably used as a polymer suitable for hair-care products in an amount of 0.1 to 10% by weight in well-known compositions such as shampoos, rinses, hair treatment products, hair setting products, cold permanent wave lotions. The hair-care products into which the copolymer is incorporated may be of any forms such as liquid, cream, emulsion, gel. It may also be used in combination with well-known conventional naturally occurring polymers, modified products of naturally occurring polymers or synthetic polymers.

Hair-care products in which the copolymer in accordance with the present invention is used include hair setting compositions for setting hair in desired hair style such as aerosol hair sprays, pump hair sprays, foaming type hair sprays, hair mists, hair setting lotions, hair styling gels, hair liquids, hair creams, hair oils, and those for providing hair with softness, gloss, smooth combing, recovery from damage, manageability such as shampoos, rinses, hair treatment lotions, cold permanent wave lotions.

More particularly, typical examples of hair-care products in which the copolymers in accordance with the present invention are incorporated are as follows.

#### (1) Hair-care products for hair setting:

Hair-care products for hair setting include those in which water and/or an alcohol e.g. ethanol or isopropanol is used as a solvent known in the art such as aerosol hair spray, pump hair spray, foaming type hair spray, hair mist, hair-setting lotion, hair-styling gel, hair liquid, hair cream, hair oil.

The copolymers in accordance with the present invention are used in these hair-care products as a partial or total substitute for or in combination with anionic, nonionic, cationic and amphoteric polymers and polysiloxane polymers conventionally used in these hair-care products.

The copolymers in accordance with the present invention can also be used in hair-care products in combination with oils or fats, humectants, solubilizing agents, emulsifiers, thickeners, germicides, perfumes conventionally used in hair-care products.

For these uses, it is preferable that the copolymer comprises a unit of the hydrophilic monomer (a) in 15 to 59.5% by weight, a unit of the monomer comprising a polysiloxane group (b) in 0.5 to 45% by weight, and a unit of the hydrophobic monomer (c) in 40 to 84.5% by weight.

When the ionic natures of the hydrophilic monomer (a) are nonionic, anionic, amphoteric in that the monomer has cationic and anionic natures in its molecule, or amphoteric in that a cationic monomer and an anionic monomer are in admixture, it is preferable that a unit of the copolymer comprises the hydrophilic monomer (a) in 20 to 59.5% by weight, a unit of the monomer comprising a polysiloxane group (b) in 0.5 to 40% by weight, and a unit of the hydrophobic monomer (c) in 40 to 79.5% by weight.

When the hydrophilic monomer (a) is cationic, it is preferable that the copolymer comprises a unit of the hydrophilic monomer (a) in 15 to 54.5% by weight, a unit of the monomer comprising a polysiloxane group (b) in 0.5 to 45% by weight, and a unit of the hydrophobic monomer (c) in 40 to 84.5% by weight.

When the hydrophilic monomer (a) is amphoteric in that a cationic monomer and an anionic monomer are in admixture, the ratio by weight of cationic monomer units/anionic monomer units is preferably 1/9 to 9/1.

#### (2) Hair-care products for hair conditioning

Hair-care products for hair conditioning include those in which water and/or an alcohol, e.g. ethanol or isopropanol is used as a solvent such as shampoos, hair rinses, cold permanent wave lotions and those in which water and/or an alcohol e.g. ethanol or isopropanol, or an alcohol and/or a hydrocarbon of a boiling point of 50 to 300°C such as hair treatment products.

When the hair-care products are shampoos in which the copolymers in accordance with the present invention are used, it is a conventional practice to use in the shampoos anionic, amphoteric or nonionic surfactants, and it is also possible to use in the shampoos foam improvers, thickeners, hydrotropes, emulsifiers, conditioning aids, germicides, perfumes.

When the hair-care products are hair-rinses in which the copolymers in accordance with the present invention are used, it is a conventional practice to use in the rinses cationic surfactants, and it is also possible to use in the rinses oils and fats, cationic surfactants, amphoteric surfactants, humectants, solubilizing agents, emulsifiers, thickeners, germicides, hair tonics, perfumes.

When the hair-care products are cold permanent wave lotions, it is a conventional practice to use in the lotions bromates, perborates, oxidation-reduction compositions e.g. thioglycolates or cysteine and the like. It is also possible to use in the lotion surfactants, thickeners, stabilizing agents, emulsifiers, conditioning aids, humectants, germicides, perfumes.

When the hair-care products are hair treatment products, the copolymers in accordance with the present invention are used in these hair treatment products as a partial or total substitute for or in combination with cationic surfactants and/or cationic polymers e.g. cationic polypeptides, cationic celluloses, cationic polysiloxanes. It is also possible to use in the hair treatment products oils and fats, amphoteric polymers, humectants, solubilizing agents, emulsifiers, thickeners, germicides, hair tonics, perfumes.

The copolymers in accordance with the invention when they are used in the hair treatment products are preferably such that the hydrophilic monomer (a) is cationic, amphoteric in that it has cationic and anionic natures in its molecule, or amphoteric in that a cationic monomer and an anionic monomer are in admixture. The hydrophilic monomers (a) may be used singly or in combination, but the ratio by weight of the units of a cationic hydrophilic monomer/the units of an anionic or amphoteric hydrophilic monomer which has anionic and cationic natures in its molecule is 1/9 to 9/1.

The copolymers in accordance with the present invention preferably comprises a unit of the hydrophilic monomer (a) in 30 to 99.5% by weight, a unit of the monomer comprising a polysiloxane group (b) in 0.5 to 70% by weight, and a unit of the hydrophobic monomer in 0 to 69.5% by weight. Specific embodiments are disclosed in the appended claims.

### [III] Examples

The present invention is explained more specifically with reference to the following preparation examples and formulation examples without limit thereto. The parts and percentages in the preparation examples are represented by weight. The parts and percentages in the formulation examples are represented by weight on the basis of effective components.

#### Preparation Example 1

In a five-neck flask equipped with a reflux condenser, a dropping funnel, a thermometer, a glass tube for nitrogen substitution and a stirrer are charged 70 parts of dimethylaminoethyl methacrylate, 25 parts of N-vinylpyrrolidone, 5 parts of polysiloxane FM0721 and 150 parts of anhydrous ethanol. A 0.6 part amount of azobisisobutyronitrile is added to the mixture, and the polymerization is carried out for 8 hours by heating under reflux at 80°C under a nitrogen stream.

Next, a 50% solution in anhydrous alcohol of propanesultone which is equimolar to the dimethylaminoethyl methacrylate is added dropwise from a dropping funnel into the five-neck flask and heated under reflux at 80°C for further 6 hours under a nitrogen stream in order to conduct amphoterization reaction. The polymer thus obtained is referred to as "P-1". In an actual practice, the polymer thus obtained had an average molecular weight of 170,000.

#### Preparation Example 2

In a five-neck flask similar to that in Preparation Example 1 are charged 30 parts of dimethylaminoethyl methacrylate, 70 parts of polysiloxane FM0711 and 200 parts of anhydrous ethanol. One part of azobisisobutyronitrile is added to the mixture, and the polymerization is carried out for 6 hours by heating under reflux at 80°C under a nitrogen stream.

Next, a 50% solution in anhydrous ethanol of propanesultone which is equimolar to the dimethylaminoethyl methacrylate is added dropwise from a dropping funnel into the five-neck flask and heated under reflux at 80°C under a nitrogen stream in order to conduct cationization reaction for further 6 hours. The polymer thus obtained is referred to as "P-2". In an actual practice, the polymer obtained had an average molecular weight of 25,000.

#### Preparation Example 3

In a five-neck flask similar to that in Preparation Example 1 are charged 85 parts of dimethylaminoethyl methacrylate, 11 parts of lauryl methacrylate, 3 parts of polysiloxane FM0725, 1 part of polysiloxane FP-2231 and 67 parts of anhydrous ethanol, and the mixture is heated under reflux at 80°C under a nitrogen stream. A solution of 0.6 part of azobisisobutyronitrile in 33 parts of ethanol is added to a five-neck flask by dropping from a dropping funnel over a period of 3 hours. Next, 0.3 part of azobisisobutyronitrile was added to the mixture, and the polymerization is carried out for further 6 hours by heating under reflux at 80°C under a nitrogen stream.

Next, a 40% solution in anhydrous ethanol of an aminomethylpropanol neutralization product of monochloroacetic acid which is equimolar to the dimethylaminoethyl methacrylate is added dropwise from a dropping funnel into the five-neck flask and heated under reflux at 80°C for further 6 hours under a nitrogen stream in order to conduct amphoterization reaction.

Then, ethanol is removed by heating while pure water is added by from a dropping funnel to the five-neck flask so as to give an aqueous solution of the polymer. The polymer thus obtained is referred to as "P-3". In an actual practice the polymer obtained had an average molecular weight of 300,000.

#### Preparation Example 4

In a five-neck flask similar to that in Preparation Example 1 are charged 40 parts of dimethylaminoethyl methacrylate, 35 parts of t-butyl methacrylate, 24 parts of tridecyl methacrylate, 1 part of polysiloxane FM0721 and 150 parts of anhydrous ethanol. 0.6 part of azobisisobutyronitrile is added, and the polymerization is carried out for 8 hours by heating under reflux at 80°C under a nitrogen stream.

Next, a 40% solution in anhydrous ethanol of a potassium hydroxide neutralization product of monochloroacetic acid which is equimolar to the dimethylaminoethyl methacrylate is added dropwise from a dropping funnel into the five-neck flask and heated under reflux at 80°C for further 12 hours under a nitrogen stream in order to conduct amphoterization reaction.

Suspended materials (potassium chloride) are removed by pressurized filtration from the viscous suspension thus obtained.

The filtrate is passed through a column in which a cation exchange resin ("DIAION PK-220", of which system has been substituted by anhydrous ethanol after regeneration) has been packed and is passed through a column in which an anion exchange resin ("DIAION PA-416", of which system has been substituted by anhydrous ethanol after regeneration) has been packed. The polymer thus obtained is referred to as "P-4". In an actual practice, the polymer obtained had an average molecular weight of 60,000.

#### Preparation Example 5

In a five-neck flask similar to that in Preparation Example 1 are charged 70 parts of N-vinylpyrrolidone, 30 parts of polysiloxane FM0721 and 100 parts of anhydrous ethanol, and 0.6 part of azobisisobutyronitrile is added to the mixture. The polymerization is carried out for 8 hours by heating under reflux at 80°C under a nitrogen stream.

The polymer thus obtained is referred to as "P-5". In an actual practice, the polymer obtained had an average molecular weight of 150,000.

#### Preparation Example 6

In a five-neck flask similar to that in Preparation Example 1 are charged 15 parts of acrylic acid, 5 parts of methacrylic acid, 10 parts of methyl acrylate, 40 parts of butyl methacrylate, 25 parts of lauryl methacrylate, 5 parts of polysiloxane FM0721 and 150 parts of anhydrous ethanol. 0.6 part of benzoyl peroxide is added, and the polymerization is carried out for 6 hours by heating under reflux at 80°C under a nitrogen stream.

Next, a 50% solution in anhydrous ethanol of triethanolamine which corresponds to 85% molar amount of the acid is added dropwise under cooling from a dropping funnel into the five-neck flask. The polymer thus obtained is referred to as "P-6". In an actual practice, the polymer obtained had an average molecular weight of 120,000.

#### Preparation Example 7

In a five-neck flask similar to that in Preparation Example 1 are charged 45 parts of methacrylic acid, 10 parts of methyl methacrylate, 30 parts of iso-butyl methacrylate, 15 parts of palmityl methacrylate and 150 parts of toluene. 0.6 part of benzoyl peroxide is added, and the polymerization is carried out for 6 hours by heating under reflux at 80°C under a nitrogen stream.

Next, 1 part of benzyltrimethylammonium chloride is added, and 5 parts of polysiloxane FM-0521 is added dropwise from a dropping funnel into the five-neck flask in order to conduct addition reaction by heating under reflux at 80°C for 6 hours under a nitrogen stream.

Toluene in the toluene solution obtained is removed by evaporation by heating to give a precursor polymer as a solid. The polymer is dissolved in a 5% water-containing ethanol so that it has a concentration of 40%.

Next, a 50% solution in ethanol (containing 5% of water) of aminomethylpropanol which corresponds to 85% molar amount of the residual acid is added dropwise under cooling from a dropping funnel into the five-neck flask. The polymer thus obtained is referred to as "P-7". In an actual practice, the polymer obtained had an average molecular weight of

90,000.

Formulation Example 1

A shampoo composition having the following formulation was prepared.

Sodium polyoxyethylenelauryl sulfate (3EO)	16%
Lauroyl diethanolamide	2%
"P-1"	1.5%
Perfume	0.2%
Preservative	0.1%
Coloring matter	trace
Pure water	balance
	<u>100%</u>

When the composition was used for shampoos, hair after washing was combed smoothly, and the hair after drying had an excellent gloss and brilliance and a smooth feeling so that the hair was combed smoothly.

With repeated shampoos, adverse effects such as tackiness were not observed.

Formulation Example 2

A shampoo composition having the following formulation was prepared.

Sodium polyoxyethylenelauryl sulfate (3EO)	10%
Sodium lauryl sulfate	8%
Lauroyl diethanolamide	2%
"P-3"	1.5%
Pure water	<u>balance</u>
	100%

When the composition was used for shampoos, excellent effects as in Formulation Example 1 were obtained.

Formulation Example 3

A shampoo composition having the following formulation was prepared.

Coconut oil fatty acid dimethylaminosulfobetaine	10%
Sodium polyoxyethylenelauryl sulfate (3EO)	5%
"P-5"	0.5%
Pure water	balance
	<u>100%</u>

When the composition was used for shampoos, excellent effects as in Example 1 was obtained.

Formulation Example 4

A rinse composition having the following formulation was prepared.

Stearyltrimethylammonium chloride	1.5%
Cetanol	2%
"P-2"	0.2%

(continued)

Perfume	0.2%
Pure water	balance
	100%

When the composition was used for a rinse, hair after rinsing was combed smoothly, and the hair after drying had an excellent gloss and brilliance and a smooth feeling so that the hair was combed smoothly.

With repeated rinsings, adverse effects such as tackiness were not observed.

#### Formulation Example 5

A hair oil composition having the following formulation was prepared.

Octamethylcyclotetrasiloxane	40%
"P-2"	8%
Anhydrous ethanol	<u>balance</u>
	100%

When the composition was used for a rinse, hair after rinsing was combed smoothly, and the hair after drying had an excellent gloss and brilliance and a smooth feeling so that the hair was combed smoothly. When the hair oil composition was applied to hair and the hair was washed in repeated cycle, adverse effects such as tackiness or development of a feeling of physical disorder due to its accumulation were not observed.

#### Formulation Example 6

A diluted polymer solution of the following formulation was charged in a spraying can, which were then charged with a liquefied petroleum gas to prepare a hair spray composition.

A diluted polymer solution	
"P-2"	4 parts
Anhydrous ethanol	balance
	<u>65 parts</u>

Liquefied petroleum gas	
(3 kg/cm <sup>2</sup> G, 20°C)	35 parts

When the composition was used by spraying it onto hair, it afforded the hair an excellent set maintaining capability as well as an excellent gloss and brilliance and a smooth feeling. When the hair oil composition was applied to hair and the hair was washed in repeated cycle, adverse effects such as tackiness or a feeling of physical disorder due to its accumulation were not observed.

#### Formulation Example 7

In the same manner as in Formulation Example 6, a hair spray composition was prepared.

A diluted polymer solution	
"P-6"	3 parts
Anhydrous ethanol	balance
	<u>70 parts</u>

Liquefied petroleum gas	
(3 kg/cm <sup>2</sup> G, 20°C)	30 parts

When the composition was used by spraying it onto hair, an excellent effect like the Example 6 was obtained.

#### Formulation Example 8

In the same manner as in Formulation Example 6, a foaming aerosol composition was prepared.

A diluted polymer solution	
"P-4"	2 parts
YUKAFOMER AM-75R 205S*	2 parts
Polyoxyethylene cetyl ether (10EO)	0.3 parts
Polyoxyethylene cetyl ether (2EO)	0.1 parts
Pure water	balance
	88 parts

\*YUKAFOMER AM-75R 205S\* is a carboxybetaine type amphoteric polymer which is commercially available from MITSUBISHI PETROCHEMICAL CO., LTD.

Liquefied petroleum gas	
(3 kg/cm <sup>2</sup> G, 20°C)	12 parts

When the composition was used by applying it to hair, an excellent effect like the Formulation Example 6 was obtained.

#### Formulation Example 9

A hair set lotion composition having the following formulation was prepared.

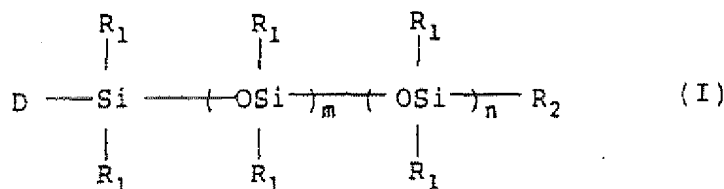
"P-4"	3%
Pure water	60%
Anhydrous ethanol	balance
	100%

When the composition was used by spraying it onto hair, an excellent effect like the Formulation Example 6 was obtained.

#### Claims

1. Use in a hair-care product of a copolymer comprising (a) a unit of a hydrophilic ethylenically unsaturated monomer in a quantity of 15 to 99.9% by weight; (b) a unit of an ethylenically unsaturated monomer having a polysiloxane group in a quantity of 0.1 to 85% by weight; and (c) a unit of a hydrophobic ethylenically unsaturated monomer in a quantity of 0 to 84.9% by weight.
2. Use in a hair-care product according to claim 1, wherein the ethylenically unsaturated monomer having a polysiloxane group (b) comprises one or more of the monomers represented by the formula (I):





wherein D, R<sub>1</sub>, R<sub>2</sub>, m and n have the following meanings, respectively:

D = an unsaturated group having radical polymerizability selected from the group consisting of a vinyl group, a vinylalkylene group, a vinylhydroxyalkylene group, an acryloyloxyalkylene group, a methacryloyloxyalkylene group, an acryloyloxyhydroxyalkylene group and a methacryloyloxyhydroxyalkylene group;

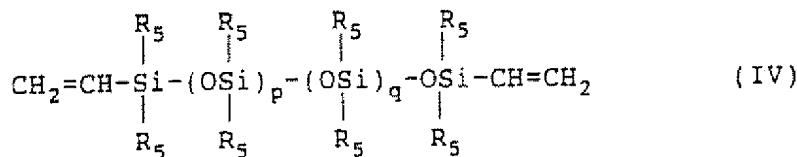
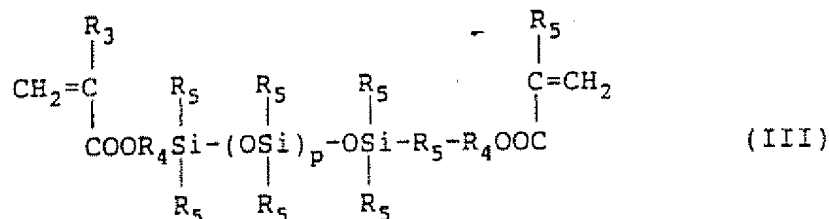
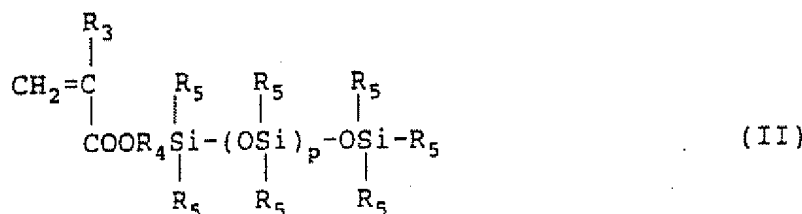
R<sub>1</sub> = a hydrogen atom, a phenyl group, an alkyl group having 1 to 10 carbon atoms, a polyalkylene group, a polyoxyalkylene group of which end has been substituted by an ether or ester group, a polyalkylenepolyamine group, a fatty acid group or a polysiloxane group, respectively;

R<sub>2</sub> = a hydrogen atom, a phenyl group, an alkyl group having 1 to 10 carbon atoms, a polyalkylene group, a polyoxyalkylene group of which end has been substituted by an ether or ester group, a polyalkylenepolyamine group, a fatty acid group or a polysiloxane group, or an unsaturated group having radical polymerizability selected from the group consisting of a vinyl group, a vinylalkylene group, a vinylhydroxyalkylene group, an acryloyloxyalkylene group or a methacryloyloxyalkylene group;

m = an integer from 4 to 150; and

n = an integer from 0 to 150, wherein the sum of m and n is within 150.

3. Use in a hair-care product according to claim 1, wherein the ethylenically unsaturated monomer having a polysiloxane group (b) comprises one or a mixture of the two or more of the monomers represented by the formulae (II) to (IV):



wherein R<sub>3</sub> to R<sub>5</sub>, p and q have the following meanings independently of each other between the formulae:

R<sub>3</sub> = a hydrogen atom or a methyl group;

R<sub>4</sub> = an alkylene group having 1 to 4 carbon atoms;

R<sub>5</sub> = an alkyl group having 1 to 10 carbon atoms or a phenyl group;

p = an integer of 1 or more; and

q = an integer of 1 or more, wherein the sum of p and q are within 150.

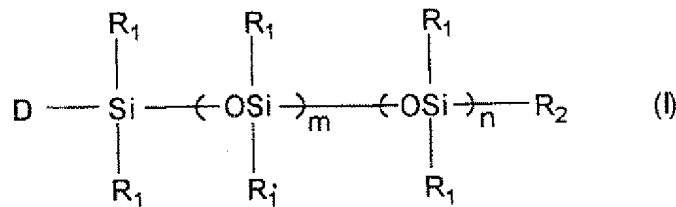
4. Use in a hair-care product according to claim 1, wherein the hydrophilic unsaturated monomer (a) comprises a nonionic unsaturated monomer.
5. Use in a hair-care product according to claim 1, wherein the hydrophilic monomer (a) comprises an anionic unsaturated monomer.
6. Use in a hair-care product according to claim 1, wherein the hydrophilic monomer (a) comprises a cationic unsaturated monomer.
7. Use in a hair-care product according to claim 1, wherein the hydrophilic unsaturated monomer (a) comprises an amphoteric unsaturated monomer in that the monomer has an anionic nature and a cationic nature in its molecule.
8. Use in a hair-care product according to claim 1, wherein the hydrophilic unsaturated monomer (a) comprises a mixture of at least two of monomers consisting of a nonionic unsaturated monomer, an anionic unsaturated monomer, a cationic unsaturated monomer, and an amphoteric unsaturated monomer in that the monomer has an anionic nature and a cationic nature in its molecule.
9. Use in a hair-care product according to claim 1, wherein the copolymer comprises (a) a unit of a hydrophilic unsaturated monomer selected from the group consisting of a nonionic monomer, an anionic monomer, an amphoteric monomer in that the monomer has an anionic nature and a cationic nature in its molecule, and a mixture thereof, in a quantity of 20 to 59.5% by weight; (b) a unit of an unsaturated monomer having a polysiloxane group, in a quantity of 0.5 to 40% by weight; and (c) a unit of a hydrophobic unsaturated monomer, in a quantity of 40 to 79.5% by weight, the polymer being suitable for use in hair-setting.
10. Use in a hair-care product according to claim 1, wherein the copolymer comprises (a) a unit of a hydrophilic monomer which is a mixture of a cationic unsaturated monomer and an anionic unsaturated monomer, the weight ratio of the cationic monomer to the anionic monomer being 1/9 to 9/1, in a quantity of 20 to 59.5% by weight, (b) a unit of the unsaturated monomer having a polysiloxane group, in a quantity of 0.5 to 40% by weight; and (c) a unit of a hydrophobic unsaturated monomer, in a quantity of 40 to 79.5% by weight, the polymer being suitable for hair setting.
11. Use in a hair-care product according to claim 1, wherein the copolymer comprises (a) a unit of a hydrophilic unsaturated monomer which is cationic, in a quantity of 15 to 54.5% by weight; (b) a unit of an unsaturated monomer having a polysiloxane group, in a quantity of 0.5 to 45% by weight; and (c) a unit of a hydrophobic unsaturated monomer, in a quantity of 40 to 84.5% by weight, the polymer being suitable for hair setting.
12. Use in a hair-care product according to claim 1, wherein the copolymer comprises (a) a unit of a hydrophilic unsaturated monomer, in a quantity of 15 to 99.5% by weight, (b) a unit of an unsaturated monomer having a polysiloxane group, in a quantity of 0.5 to 20% by weight and (c) a unit of a hydrophobic unsaturated monomer, in a quantity of 0 to 84.5% by weight.
13. Use in a hair-care product according to claim 1, wherein the copolymer comprises (a) a unit of a hydrophilic unsaturated monomer which is a cationic monomer or an amphoteric monomer in that the monomer has an anionic nature and a cationic nature in its molecule, in a quantity of 30 to 99.5% by weight; (b) a unit of an unsaturated monomer having a polysiloxane group, in a quantity of 0.5 to 70% by weight; and (c) a unit of a hydrophobic unsaturated monomer, in a quantity of 0 to 69.5% by weight, the polymer being suitable for hair conditioning.
14. Use in a hair-care product according to claim 1, wherein the copolymer comprises (a) a unit of a hydrophilic monomer which is a combination of a cationic monomer and an anionic monomer or which is a combination of a cationic monomer and an amphoteric monomer in that the monomer has an anionic nature and a cationic nature in its molecule, the weight ratio of the cationic monomer to the anionic monomer or to the amphoteric monomer being 1/9 to 9/1, in a quantity of 30 to 99.5% by weight; (b) a unit of an unsaturated monomer having a polysiloxane group, in a quantity of 0.5 to 70% by weight; and (c) a unit of hydrophobic unsaturated monomer, in a quantity of 0 to 69.5% by weight, the polymer being suitable for hair conditioning.
15. A hair-care product comprising a copolymer comprising (a) a unit of a hydrophilic ethylenically unsaturated monomer in a quantity of 15 to 99.9% by weight; (b) a unit of an ethylenically unsaturated monomer having a polysiloxane group in a quantity of 0.1 to 85% by weight; and (c) a unit of an hydrophobic ethylenically unsaturated

monomer in a quantity of 0 to 84.9% by weight, which copolymer is dissolved in water and/or an alcohol in a concentration of 0.5 to 10% by weight.

16. A hair-care product according to claim 15, comprising the copolymer dissolved in a concentration of 0.5 to 10% by weight in a hydrocarbon of a boiling temperature of 50 to 300°C or in a mixture of the hydrocarbon with an alcohol.

#### Patentansprüche

1. Verwendung eines Copolymeren, das (a) eine Einheit aus einem hydrophilen ethylenartig ungesättigten Monomeren in einer Menge von 15 bis 99,9 Gew.%; (b) eine Einheit aus einem ethylenartig ungesättigten Monomeren, das eine Polysiloxangruppe hat, in einer Menge von 0,1 bis 85 Gew.%; und (c) eine Einheit aus einem hydrophoben ethylenartig ungesättigten Monomeren in einer Menge von 0 bis 84,9 Gew.% enthält, in einem Haarpflegeprodukt.
2. Verwendung in einem Haarpflegeprodukt nach Anspruch 1, wobei das ethylenartig ungesättigte Monomer, das eine Polysiloxangruppe hat, (b) ein oder mehrere Monomere, die durch die Formel (I) dargestellt werden, enthält:



worin D, R<sub>1</sub>, R<sub>2</sub>, m und n jeweils die folgenden Bedeutungen haben:

D = eine ungesättigte Gruppe mit radikalischer Polymerisierbarkeit, die aus der aus einer Vinylgruppe, einer Vinylalkylengruppe, einer Vinylhydroxyalkylengruppe, einer Acryloyloxyalkylengruppe, einer Methacryloyloxyalkylengruppe, einer Acryloyloxyhydroxyalkylengruppe und einer Methacryloyloxyhydroxyalkylengruppe bestehenden Gruppe ausgewählt ist;

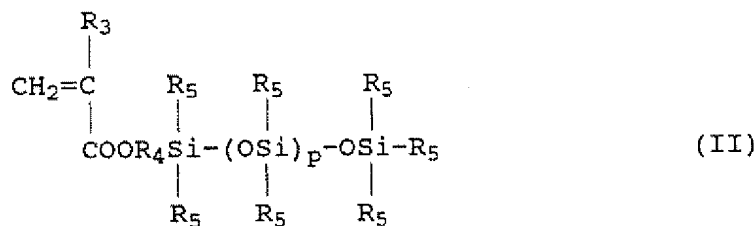
R<sub>1</sub> = jeweils ein Wasserstoffatom, eine Phenylgruppe, eine Alkylgruppe mit 1 bis 10 Kohlenstoffatomen, eine Polyalkylengruppe, eine Polyoxyalkylengruppe, deren Ende mit einer Ether- oder Estergruppe substituiert worden ist, eine Polyalkylenpolyaminygruppe, eine Fettsäuregruppe oder eine Polysiloxangruppe;

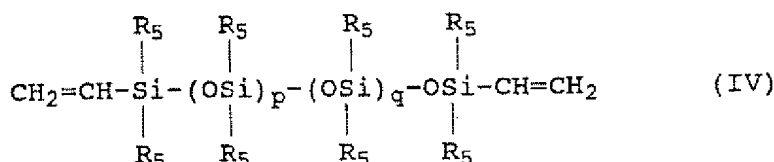
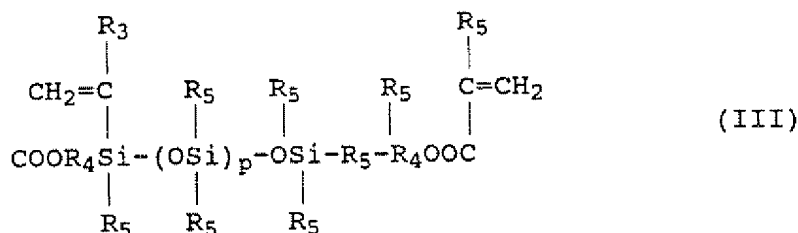
R<sub>2</sub> = ein Wasserstoffatom, eine Phenylgruppe, eine Alkylgruppe mit 1 bis 10 Kohlenstoffatomen, eine Polyalkylengruppe, eine Polyoxyalkylengruppe, deren Ende mit einer Ether- oder Estergruppe substituiert worden ist, eine Polyalkylenpolyaminygruppe, eine Fettsäuregruppe oder eine Polysiloxangruppe oder eine ungesättigte Gruppe mit radikalischer Polymerisierbarkeit, die aus der aus einer Vinylgruppe, einer Vinylalkylengruppe, einer Vinylhydroxyalkylengruppe, einer Acryloyloxyalkylengruppe oder einer Methacryloyloxyalkylengruppe bestehenden Gruppe ausgewählt ist;

m = eine ganze Zahl zwischen 4 und 150; und

n = eine ganze Zahl zwischen 0 und 150, wobei die Summe aus m und n im Zahlenbereich bis 150 liegt.

3. Verwendung in einem Haarpflegeprodukt nach Anspruch 1, wobei das ethylenartig ungesättigte Monomer, das eine Polysiloxangruppe hat, (b) eine Monomer oder ein Gemisch aus zwei oder mehreren Monomeren, das (die) durch die Formeln (II) bis (IV) dargestellt wird (werden), enthält:





worin  $\text{R}_3$  bis  $\text{R}_5$ ,  $p$  und  $q$  unabhängig voneinander in den einzelnen Formeln die folgenden Bedeutungen haben:

- $\text{R}_3$  = ein Wasserstoffatom oder eine Methylgruppe;  
 $\text{R}_4$  = eine Alkylengruppe mit 1 bis 4 Kohlenstoffatomen;  
 $\text{R}_5$  = eine Alkylgruppe mit 1 bis 10 Kohlenstoffatomen oder eine Phenylgruppe;  
 $p$  = eine ganze Zahl 1 oder mehr; und  
 $q$  = eine ganze Zahl 1 oder mehr, wobei die Summe aus  $p$  und  $q$  im Zahlenbereich bis 150 liegt.

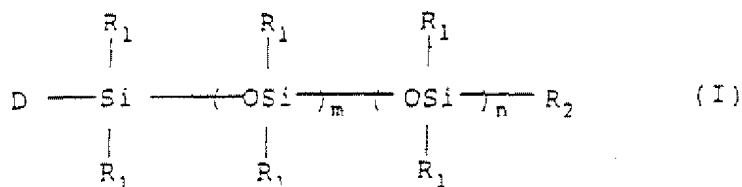
4. Verwendung in einem Haarpflegeprodukt nach Anspruch 1, wobei das hydrophile ungesättigte Monomer (a) ein nichtionisches ungesättigtes Monomer umfaßt.
5. Verwendung in einem Haarpflegeprodukt nach Anspruch 1, wobei das hydrophile Monomer (a) ein anionisches ungesättigtes Monomer umfaßt.
6. Verwendung in einem Haarpflegeprodukt nach Anspruch 1, wobei das hydrophile Monomer (a) ein kationisches ungesättigtes Monomer umfaßt.
7. Verwendung in einem Haarpflegeprodukt nach Anspruch 1, wobei das hydrophile ungesättigte Monomer (a) ein amphoterer ungesättigtes Monomer umfaßt, in dem das Monomer in seinem Molekül eine anionische Natur und eine kationische Natur aufweist.
8. Verwendung in einem Haarpflegeprodukt nach Anspruch 1, wobei das hydrophile ungesättigte Monomer (a) ein Gemisch aus mindestens zwei Monomeren, die aus einem nicht-ionischen ungesättigten Monomeren, einem anionischen Monomeren, einem kationischen ungesättigten Monomeren und einem amphoteren ungesättigten Monomeren, wobei dieses Monomer in seinem Molekül eine anionische Natur und eine kationische Natur aufweist, bestehen, umfaßt.
9. Verwendung in einem Haarpflegeprodukt nach Anspruch 1, wobei das Copolymer (a) eine Einheit aus einem hydrophilen ungesättigten Monomeren, das aus der aus einem nicht-ionischen Monomeren, einem anionischen Monomer, einem amphoteren Monomer, das in seinem Molekül eine anionische Natur und eine kationische Natur aufweist, bestehenden Gruppe ausgewählt ist, in einer Menge von 20 bis 59,5 Gew.%; (b) eine Einheit aus einem ungesättigten Monomeren, das eine Polysiloxangruppe hat, in einer Menge von 0,5 bis 40 Gew.%; und (c) eine Einheit aus einem hydrophoben ungesättigten Monomeren in einer Menge von 40 bis 79,5 Gew.% enthält, und das Polymer zur Verwendung beim Haarfestigen geeignet ist.
10. Verwendung eines Haarpflegeprodukt nach Anspruch 1, wobei das Copolymer (a) eine Einheit aus einem hydrophilen ungesättigten Monomeren, das ein Gemisch aus einem kationischen ungesättigten Monomeren und einem anionischen ungesättigten Monomeren ist, und in dem das Gewichtsverhältnis des kationischen Monomeren zu dem anionischen Monomeren zwischen 1/9 und 9/1 liegt, in einer Menge von 20 bis 59,9 Gew.%; (b) eine Einheit aus dem ungesättigten Monomeren, das eine Polysiloxangruppe hat, in einer Menge von 0,5 bis 40 Gew.%; und (c) eine Einheit aus einem hydrophoben ungesättigten Monomeren in einer Menge von 40 bis 79,5 Gew.% enthält,

und das Polymer zum Haarfestigen geeignet ist.

11. Verwendung in einem Haarpflegeprodukt nach Anspruch 1, wobei das Copolymer (a) eine Einheit aus einem hydrophilen ungesättigten Monomeren, das kationische ist, in einer Menge von 15 bis 54,5 Gew.%; (b) eine Einheit aus einem ungesättigten Monomeren, das eine Polysiloxangruppe hat, in einer Menge von 0,5 bis 45 Gew.%; und (c) eine Einheit aus einem hydrophoben ungesättigten Monomeren in einer Menge von 40 bis 84,5 Gew.% enthält, und das Polymer zum Haarfestigen geeignet ist.
12. Verwendung eines Haarpflegeproduktes nach Anspruch 1, wobei das Copolymer (a) eine Einheit aus einem hydrophilen ungesättigten Monomeren in einer Menge von 15 bis 99,5 Gew.%; (b) eine Einheit aus einem ungesättigten Monomeren, das eine Polysiloxangruppe hat, in einer Menge von 0,5 bis 20 Gew.%; und (c) eine Einheit aus einem hydrophoben ungesättigten Monomeren in einer Menge von 0 bis 84,5 Gew.% enthält.
13. Verwendung in einem Haarpflegeprodukt nach Anspruch 1, wobei das Copolymer (a) eine Einheit aus einem hydrophilen ungesättigten Monomeren, das ein kationisches Monomer oder ein amphoterisches Monomer, in dem das Monomer eine anionische Natur und eine kationische Natur in seinem Molekül aufweist, ist, in einer Menge von 30 bis 99,5 Gew.%; (b) eine Einheit aus einem ungesättigten Monomeren, das eine Polysiloxangruppe hat, in einer Menge von 0,5 bis 70 Gew.%; und (c) eine Einheit aus einem hydrophoben ungesättigten Monomeren in einer Menge von 0 bis 69,5 Gew.% enthält, und das Polymer zum Haarkonditionieren geeignet ist.
14. Verwendung in einem Haarpflegeprodukt nach Anspruch 1, wobei das Copolymer (a) eine Einheit aus einem hydrophilen Monomeren, das eine Kombination aus einem kationischen Monomeren und einen anionischen Monomeren ist oder das eine Kombination aus einem kationischen Monomeren und einem amphoterischen Monomeren, in dem dieses Monomer eine anionische Natur und eine kationische Natur in seinem Molekül aufweist, ist, worin das Gewichtsverhältnis des kationischen Monomeren zu dem anionischen Monomeren oder zu dem amphoterischen Monomeren zwischen 1/9 und 9/1 liegt, in einer Menge von 30 bis 95 Gew.%; (b) eine Einheit aus einem ungesättigten Monomeren, das eine Polysiloxangruppe hat, in einer Menge von 0,5 bis 70 Gew.%; und (c) eine Einheit aus einem hydrophoben ungesättigten Monomeren in einer Menge von 0 bis 69,5 Gew.% enthält, und das Polymer zur Haarkonditionierung geeignet ist.
15. Haarpflegeprodukt, das ein Copolymer enthält, welches (a) eine Einheit aus einem hydrophilen ethylenartig ungesättigten Monomeren in einer Menge von 15 bis 99,9 Gew.%; (b) eine Einheit aus einem ethylenartig ungesättigten Monomeren, das eine Polysiloxangruppe hat, in einer Menge von 0,1 bis 85 Gew.%; und (c) eine Einheit aus einem hydrophoben ethylenartig ungesättigten Monomeren in einer Menge von 0 bis 84,9 Gew.% umfaßt, und in dem das Copolymer in einer Konzentration von 0,5 bis 10 Gew.% in Wasser und/oder einem Alkohol aufgelöst ist.
16. Haarpflegeprodukt nach Anspruch 15, das das Copolymer, das in einer Konzentration von 0,5 bis 10 Gew.% in einem Kohlenwasserstoff mit einer Siedetemperatur zwischen 50 und 300°C oder in einem Gemisch des Kohlenwasserstoffs mit einem Alkohol aufgelöst ist, enthält.

## Revendications

1. Utilisation, dans un produit pour les soins des cheveux, d'un copolymère comprenant (a) un motif d'un monomère hydrophile à insaturation éthylénique en une quantité de 15 à 99,9 % en poids; (b) un motif d'un monomère à insaturation éthylénique ayant un groupe polysiloxane, en une quantité de 0,1 à 85 % en poids; et (c) un motif d'un monomère hydrophobe à insaturation éthylénique en une quantité de 0 à 84,9 % en poids.
2. Utilisation, dans un produit pour les soins des cheveux selon la revendication 1, dans laquelle le monomère à insaturation éthylénique ayant un groupe polysiloxane (b) comprend un ou plusieurs des monomères représentés par la formule (I) :



dans laquelle D, R<sub>1</sub>, R<sub>2</sub>, m et n ont respectivement les significations suivantes :

D est un groupe insaturé pouvant être polymérisé par polymérisation radicalaire, choisi parmi l'ensemble comprenant le groupe vinyle, les groupes vinylalkylène, les groupes vinylhydroxyalkylène, les groupes acryloyloxyalkylène, les groupes méthacryloyloxyalkylène, les groupes acryloyloxyhydroxyalkylène et les groupes méthacryloyloxyhydroxyalkylène ;

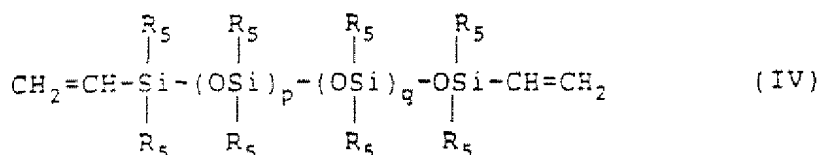
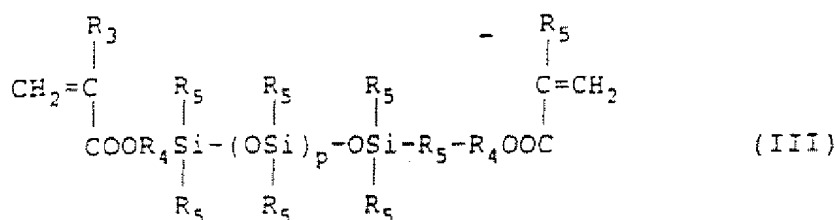
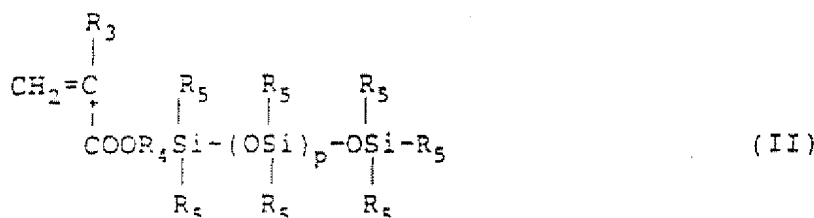
R<sub>1</sub> est un atome d'hydrogène, un groupe phényle, un groupe alkyle ayant de 1 à 10 atomes de carbone, un groupe polyalkylène, un groupe polyoxyalkylène dont l'extrémité a été remplacée par un groupe éther ou ester, un groupe polyalkylènapolyamine, un groupe acide gras ou un groupe polysiloxane, respectivement ;

R<sub>2</sub> est un atome d'hydrogène, un groupe phényle, un groupe alkyle ayant de 1 à 10 atomes de carbone, un groupe polyalkylène, un groupe polyoxyalkylène dont l'extrémité a été remplacée par un groupe éther ou ester, un groupe polyalkylènapolyamine, un groupe acide gras ou un groupe polysiloxane, ou encore un groupe insaturé polymérisable par polymérisation radicalaire, choisi parmi l'ensemble comprenant le groupe vinyle, les groupes vinylalkylène, les groupes vinylhydroxyalkylène, les groupes acryloyloxyalkylène et les groupes méthacryloyloxyalkylène ;

m est un entier de 4 à 150 ; et

n est un entier de 0 à 150, la somme de m et de n étant inférieure ou égale à 150.

3. Utilisation, dans un produit pour les soins des cheveux selon la revendication 1, où le monomère à insaturation éthylénique ayant un groupe polysiloxane (b) comprend l'un des monomères ou un mélange d'au moins deux des monomères représentés par les formules (II) à (IV) :



dans lesquelles R<sub>3</sub> à R<sub>5</sub>, p et q ont les significations suivantes, indépendamment les uns des autres entre les différentes formules :

R<sub>3</sub> est un atome d'hydrogène ou un groupe méthyle ;

R<sub>4</sub> est un groupe alkylène ayant de 1 à 4 atomes de carbone ;

R<sub>5</sub> est un groupe alkyle ayant de 1 à 10 atomes de carbone ou un groupe phényle ;

p est un entier valant 1 ou plus ; et

q est un entier valant 1 ou plus, la somme de p et de q étant inférieure ou égale à 150.

4. Utilisation dans un produit pour les soins des cheveux selon la revendication 1, dans laquelle le monomère à insaturation hydrophile (a) comprend un monomère insaturé nonionique.

5. Utilisation dans un produit pour les soins des cheveux selon la revendication 1, dans laquelle le monomère hydrophile (a) comprend un monomère insaturé anionique.
6. Utilisation dans un produit pour les soins des cheveux selon la revendication 1, dans laquelle le monomère hydrophile (a) comprend un monomère insaturé cationique.
7. Utilisation dans un produit pour les soins des cheveux selon la revendication 1, dans laquelle le monomère insaturé hydrophile (a) comprend un monomère insaturé amphotère, en ce sens que le monomère a dans sa molécule une nature anionique et une nature cationique.
8. Utilisation dans un produit pour les soins des cheveux selon la revendication 1, dans laquelle le monomère insaturé hydrophile (a) comprend un mélange d'au moins deux monomères, constitué d'un monomère insaturé nonionique, d'un monomère insaturé anionique, d'un monomère insaturé cationique et d'un monomère insaturé amphotère, en ce sens que le monomère a une nature anionique et une nature cationique dans sa molécule.
9. Utilisation dans un produit pour les soins des cheveux selon la revendication 1, dans laquelle le copolymère comprend (a) un motif d'un monomère insaturé hydrophile choisi parmi l'ensemble comprenant les monomères nonioniques, les monomères anioniques, les monomères amphotère en ce sens que les monomères ont dans leur molécule une nature anionique et une nature cationique, et leurs mélanges, en une quantité de 20 à 59,5 % en poids ; (b) un motif d'un monomère insaturé ayant un groupe polysiloxane, en une quantité de 0,5 à 40 % en poids ; et (c) un motif d'un monomère insaturé hydrophobe, en une quantité de 40 à 79,5 % en poids, le polymère convenant à une utilisation dans une mise en pli.
10. Utilisation dans un produit pour les soins des cheveux selon la revendication 1, dans laquelle le copolymère comprend (a) un motif d'un monomère hydrophile qui est un mélange d'un monomère insaturé cationique et d'un monomère insaturé anionique, le rapport pondéral du monomère cationique au monomère anionique, étant de 1/9 à 9/1, en une quantité de 20 à 59,5 % en poids, (b) un motif du monomère insaturé ayant un groupe polysiloxane, en une quantité de 0,5 à 40 % en poids ; et (c) un motif d'un monomère insaturé hydrophobe, en une quantité de 40 à 79,5 % en poids, le polymère convenant à une mise en pli.
11. Utilisation dans un produit pour les soins des cheveux selon la revendication 1, dans laquelle le copolymère comprend (a) un motif d'un monomère insaturé hydrophile qui est cationique, en une quantité de 15 à 54,5 % en poids, (b) un motif d'un monomère insaturé ayant un groupe polysiloxane, en une quantité de 0,5 à 45 % en poids ; et (c) un motif d'un monomère insaturé hydrophobe, en une quantité de 40 à 84,5 % en poids, le polymère convenant à une mise en pli.
12. Utilisation dans un produit pour les soins des cheveux selon la revendication 1, dans laquelle le copolymère comprend (a) un motif d'un monomère insaturé hydrophile, en une quantité de 15 à 99,5 % en poids, (b) un motif d'un monomère insaturé ayant un groupe polysiloxane, en une quantité de 0,5 à 20 % en poids ; et (c) un motif d'un monomère insaturé hydrophobe, en une quantité de 0 à 84,5 % en poids.
13. Utilisation dans un produit pour les soins des cheveux selon la revendication 1, dans laquelle le copolymère comprend (a) un motif d'un monomère insaturé hydrophile qui est un monomère cationique ou un monomère amphotère en ce sens que le monomère a dans sa molécule une nature anionique et une nature cationique, en une quantité de 30 à 99,5 % en poids ; (b) un motif d'un monomère insaturé ayant un groupe polysiloxane, en une quantité de 0,5 à 70 % en poids ; et (c) un motif d'un monomère insaturé hydrophobe, en une quantité de 0 à 69,5 % en poids, le polymère convenant au conditionnement des cheveux.
14. Utilisation dans un produit pour les soins des cheveux selon la revendication 1, dans laquelle le copolymère comprend (a) un motif d'un monomère hydrophile qui est une combinaison d'un monomère cationique et d'un monomère anionique, ou qui est une combinaison d'un monomère cationique et d'un monomère amphotère, en ce sens que le monomère a dans sa molécule une nature anionique et une nature cationique, le rapport pondéral du monomère cationique au monomère anionique ou au monomère amphotère étant de 1/9 à 9/1, en une quantité de 30 à 99,5 % en poids, (b) un motif d'un monomère insaturé ayant un groupe polysiloxane, en une quantité de 0,5 à 70 % en poids ; et (c) un motif d'un monomère insaturé hydrophobe, en une quantité de 0 à 69,5 % en poids, le polymère convenant au conditionnement des cheveux.
15. Produit pour les soins des cheveux, comprenant un copolymère comprenant (a) un motif d'un monomère hydrophile

à insaturation éthylénique, en une quantité de 15 à 99,9 % en poids ; (b) un motif d'un monomère à insaturation éthylénique ayant un groupe polysiloxane, en une quantité de 0,1 à 85 % en poids ; et (c) un motif d'un monomère hydrophobe à insaturation éthylénique en une quantité de 0 à 84,9 % en poids, le copolymère étant dissous dans de l'eau et/ou dans un alcool à une concentration de 0,5 à 10 % en poids.

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16. Produit pour les soins des cheveux selon la revendication 15, comprenant le copolymère dissous à une concentration de 0,5 à 10 % en poids dans un hydrocarbure ayant une température d'ébullition de 50 à 300°C, ou dans un mélange de l'hydrocarbure avec un alcool.

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**WORKS, LTD) 11-05-1977**

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**EP 0 412 707 B1**

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## Description

The present invention relates to hair care compositions which have improved hair conditioning and style retention properties while still leaving the hair with a natural non-sticky feel. These compositions utilize a group of specific silicone macromer-containing copolymers.

The desire to have hair retain a particular shape is widely held. Such style retention is generally accomplished by either of two routes: permanent chemical alteration or temporary alteration of hair style/shape. A temporary alteration is one which can be removed by water or by shampooing. Temporary style alteration has generally been accomplished by means of the application of a composition to dampened hair after shampooing and/or conditioning and prior to drying and/or styling. The materials used to provide setting benefits have generally been resins or gums and have been applied in the form of mousses, gels, lotions, or sprays. This approach presents several significant drawbacks to the user. It requires a separate step following shampooing/conditioning to apply the styling composition. In addition, since the style hold is provided by resin materials which set-up on the hair, the hair tends to feel sticky or stiff after application and it is difficult to restyle the hair without further application of the styling composition.

It has now been discovered that hair care compositions comprising certain specifically-defined silicone macromer-containing copolymers provide excellent hair style retention benefits, together with hair conditioning. The compositions may be in any of the conventional forms including, but not limited to, shampoos, conditioners, hair sprays, tonics, lotions, gels, and mousses. The compositions provide these benefits to hair without leaving the hair with a stiff or sticky/tacky feel and without negatively affecting dry hair properties, such as ease of combing. Further, hair to which the compositions of the present invention have been applied may be restyled several times without requiring reapplication of the compositions.

These results are surprising since other materials which have been typically used in hair care compositions to provide style retention, such as resins and gums, generally hurt dry hair properties (e.g., combing) and leave hair with a sticky and/or stiff feel. Furthermore, silicone materials typically used for hair conditioning tend to hurt style retention.

Siloxanes (see, for example, US-A-3,208,911, Oppliger, issued September 28, 1965) and siloxane-containing polymers have been taught for use in hair conditioning compositions. US-A-4,601,902, Fridt et al., issued July 22, 1986, describes hair conditioning or shampoo/conditioner compositions which include a polydiorganosiloxane having quaternary ammonium substituted groups attached to the silicon, and a polydiorganosiloxane having silicon-bonded substituents which are amino-substituted hydrocarbon groups. US-A-4,654,161, Kollmeier et al., issued March 31, 1987, describes a group of organopolysiloxanes containing betaine substituents. When used in hair care compositions, these compounds are said to provide good conditioning, compatibility with anionic components, hair substantivity, and low skin irritation. US-A-4,563,347, Starch, issued January 7, 1986, relates to hair conditioning compositions which include siloxane components containing substituents to provide attachment to hair. JP-A-56-129,300, Lion Corporation, published October 9, 1981, relates to shampoo conditioner compositions which include an organopolysiloxane-oxyalkylene copolymer together with an acrylic resin. US-A-4,479,893, Hirota et al., issued October 30, 1984, describes shampoo conditioner compositions containing a phosphate ester surfactant and a silicon derivative (e.g., polyether- or alcohol-modified siloxanes). JP-A-52-57337, describes hair conditioning lotions which include a copolymer of N-vinyl pyrrolidone and tris(trimethylsiloxy)vinylsilane. Polyether-modified polysiloxanes are also disclosed for use in shampoo in US-A-3,957,970, Korkis, issued May 18, 1976. US-A-4,185,087, Morlino issued January 22, 1980, describes quaternary nitrogen derivatives of trialkylamino hydroxy organosilicon compounds which are said to have superior hair conditioning properties.

Siloxane-derived materials have also been used in hair styling compositions. JP-A-56-092,811, Lion Corporation, published December 27, 1979, describes hair setting compositions which comprise an amphoteric acrylic resin, a polyoxyalkylene-denatured organopolysiloxane, and polyethylene glycol. US-A-4,744,978, Homan et al., issued May 17, 1988, describes hair styling compositions (such as hair sprays) which include the combination of a carboxyfunctional polydimethylsiloxane and a cationic organic polymer containing amine or ammonium groups. Hair styling compositions which include polydiorganosiloxanes and a cationic organic polymer are taught in US-A-4,733,677, Gee et al., issued March 29, 1988, and US-A-4,724,851, Cornwall et al., issued February 16, 1988. Finally, EP-A-117,360, Cantrell et al., published September 5, 1984, discloses compositions, containing a siloxane polymer having at least one nitrogen-hydrogen bond, a surfactant, and a solubilized titanate, zirconate or germanate, which act as both a conditioner and a hair styling aid.

Siloxane-containing polymers have also been used in non-hair care applications. US-A-4,136,250, Mueller et al., issued January 23, 1979, relates to polymeric materials used in biological contexts where oxygen permeable and tissue compatible membranes are required. They can also be used as carriers for biologically-active substances. These materials are hydrophilic water-insoluble gels which include a low molecular weight ter-

minal olefinic siloxane macromer and a polymer containing water-soluble monoolefinic monomer. US-A-4,693,935, Mazurek, issued September 15, 1987, describes pressure sensitive adhesive compositions which include a copolymer with a vinyl polymeric backbone having grafted thereto polysiloxane moieties. US-A-4,728,571, Clemens et al., issued March 1, 1988, relates to adhesive release coating compositions which comprise polysiloxane-grafted copolymers and blends of those copolymers with other polymeric materials. None of these last three patents suggest the use of the disclosed siloxane-containing polymers in hair care compositions.

It is an object of the present invention to formulate hair care compositions which provide effective hair conditioning and style retention properties.

It is also an object of the present invention to formulate hair care compositions which provide conditioning and style retention from a single composition.

It is a further object of the present invention to formulate hair care compositions which provide good style retention without leaving hair with a stiff or sticky/tacky feel.

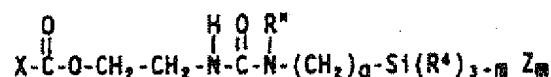
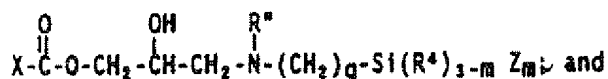
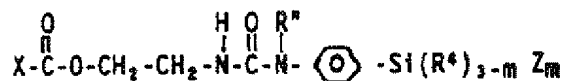
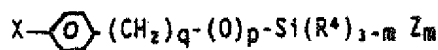
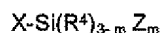
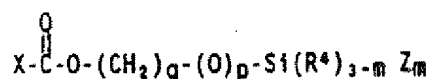
It is a further object of the present invention to provide an improved method for styling and conditioning hair.

These and other objects will become readily apparent from the detailed description which follows.

Unless otherwise indicated, all percentages and ratios herein are by weight.

According to the present invention there is provided a hair care composition comprising:

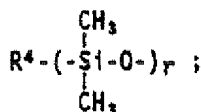
(a) from 0.1% by weight to 10.0% by weight of a silicone-containing copolymer having a molecular weight of from 10,000 to 1,000,000 comprising a component selected from: a lipophilic low polarity free radically polymerizable vinyl monomer (A), a hydrophilic polar monomer which is copolymerizable with A (B), and mixtures thereof; together with a silicone-containing macromer (C) having a weight average molecular weight of from 1,000 to 50,000 based on polydimethylsiloxane selected from



wherein m is 1, 2 or 3; p is 0 or 1; R'' is alkyl or hydrogen; q is an integer from 2 to 6; s is an integer from 0 to 2; X is



R<sup>1</sup> is hydrogen or -COOH; R<sup>2</sup> is hydrogen, methyl or -CH<sub>2</sub>COOH; Z is



R<sup>4</sup> is alkyl, alkoxy, alkylamino, aryl or hydroxyl; and r is an integer from 5 to 700;

and wherein the silicone-containing copolymer comprises from 0% to 98% by weight monomer A, from 0% to 98% by weight monomer B, and from 0.1% by weight to 50% by weight monomer C; and

(b) from 0.5% by weight to 99.5% by weight of a carrier suitable for application to hair.

The essential, as well as the optional, components of the present invention are described below.

#### Silicone-Containing Copolymer

The compositions of the present invention contain from 0.1% to 10.0%, preferably from 0.5% to 8.0%, of specifically-defined silicone-containing copolymers. It is these polymers which provide the unique hair conditioning and hair setting characteristics of the present invention. The polymers have a weight average molecular weight of from 10,000 to 1,000,000 (preferably from 30,000 to 300,000) and, preferably, have a T<sub>g</sub> of at least -20°C. As used herein, the abbreviation "T<sub>g</sub>" refers to the glass transition temperature of the non-silicone backbone, and the abbreviation "T<sub>m</sub>" refers to the crystalline melting point of the non-silicone backbone, if such a transition exists for a given polymer.

Preferred polymers comprise a vinyl polymeric backbone, preferably having a T<sub>g</sub> above -20°C and, grafted to the backbone, a polydimethylsiloxane macromer having a weight average molecular weight of from 1,000 to 50,000, preferably from 5,000 to 40,000, most preferably 20,000. The polymer is such that when it is formulated into the finished hair care composition, when dried, the polymer phase separates into a discontinuous phase which includes the polydimethylsiloxane macromer and a continuous phase which includes the backbone. It is believed that this phase separation property provides a specific orientation of the polymer on hair which results in the desired hair conditioning and setting benefits. The phase-separating nature of the compositions of the present invention may be determined as follows:

The polymer is cast as a solid film out of a good solvent (i.e., a solvent which dissolves both the backbone and the silicone). This film is then sectioned and examined by transmission electron micrography. Microphase separation is demonstrated by the observation of inclusions in the continuous phase. These inclusions should have the proper size to match the size of the silicone chain (typically a few hundred nm or less) and the proper density to match the amount of silicone present. This behavior is well documented in the literature for polymers with this structure (see, for example, S. D. Smith, Ph.D. Thesis, University of Virginia, 1987, and references cited therein).

A second method for determining phase-separating characteristics involves examining the enrichment of the concentration of silicone at the surface of a polymer film relative to the concentration in the bulk polymer. Since the silicone prefers the low energy air interface, it preferentially orients on the polymer surface. This produces a surface which is entirely covered by silicone even when the concentration of the silicone by weight in the whole polymer is low (2% to 20%). This is demonstrated experimentally by ESCA (electron spectroscopy for chemical analysis) of the dried film surface. Such an analysis shows a high level of silicone and a greatly reduced level of backbone polymer when the film surface is analyzed. (Surface here means the first few tens of Angstroms of film thickness.) By varying the angle of the interrogating beam the surface can be analyzed to varying depths.

In its broadest aspect, the copolymers utilized in the present application comprise C monomers together with monomers selected from the group consisting of A monomers, B monomers, and mixtures thereof. These copolymers contain at least A or B monomers, together with C monomers, and preferred copolymers contain A, B and C monomers.

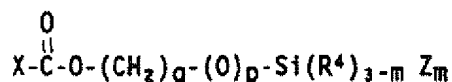
Examples of useful copolymers and how they are made are described in detail in US-A-4,696,935, Mazurek, issued September 15, 1987, and US-A-4,728,571, Clemens et al., issued March 1, 1988. These copolymers are comprised of monomers A, C and, optionally, B, which are defined as follows. A is at least one free-radically polymerizable vinyl monomer or monomers. B, when used, comprises at least one reinforcing monomer copolymerizable with A and is selected from the group consisting of polar monomers and macromers having a T<sub>g</sub> or a T<sub>m</sub> above -20°C. When used, B is up to 98%, preferably up to 80%, more preferably up to 20%, of the total monomers in the copolymer. Monomer C comprises from 0.01% to 50.0% of the total monomers in the copolymer.

Representative examples of A (hydrophobic) monomers are the acrylic or methacrylic acid esters of C<sub>1</sub>-

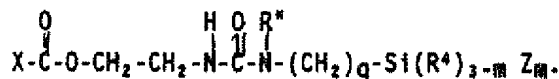
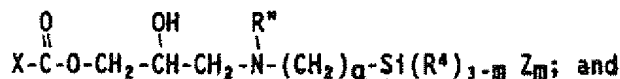
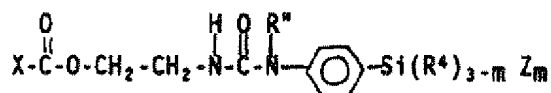
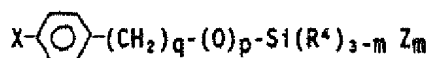
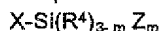
C<sub>18</sub> alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-tri-methyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, and 1-octadecanol, the alcohols having from 1-18 carbon atoms with the average number of carbon atoms being from 4-12; styrene; polystyrene macromer; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene; and mixtures thereof. Preferred A monomers include n-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, t-butylacrylate, t-butylmethacrylate, and mixtures thereof.

Representative examples of B (hydrophilic) monomers include acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butylacrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers (such as methyl vinyl ether), maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol (produced by the hydrolysis of vinyl acetate after polymerization) vinyl caprolactam, and mixtures thereof. Preferred B monomers include acrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, and mixtures thereof.

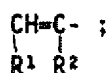
C has a weight average molecular weight of from 1,000 to 50,000, preferably from 5,000 to 40,000, most preferably from 10,000 to 20,000. The C monomer has a formula selected from the following group:



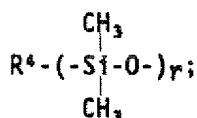
(a preferred monomer, particularly preferred when p = 0 and q = 3)



In those structures, m is 1, 2 or 3 (preferably m = 1); p is 0 or 1; R'' is alkyl or hydrogen; q is an integer from 2 to 6; s is an integer from 0 to 2; X is



R<sup>1</sup> is hydrogen or -COOH (preferably R<sup>1</sup> is hydrogen); R<sup>2</sup> is hydrogen, methyl or -CH<sub>2</sub>COOH (preferably R<sup>2</sup> is methyl); Z is



R<sup>4</sup> is alkyl, alkoxy, alkylamino, aryl, or hydroxyl (preferably R<sup>4</sup> is alkyl); and r is an integer from 5 to 700 (preferably r is about 250).

The polymers of the present invention comprise from 0% to 98% (preferably from 5% to 98%, more preferably from 50% to 90%) of monomer A, from 0% to 98% (preferably from 7.5% to 80%) of monomer B, and from 0.1% to 50% (preferably from 0.5% to 40%, most preferably from 2% to 25%) of monomer C. The combination of the A and B monomers preferably comprises from 50.0% to 99.9% (more preferably 60% to 99%, most preferably from 75% to 95%) of the polymer. The composition of any particular copolymer will help determine its formulational properties. In fact, by appropriate selection and combination of particular A, B and C components, the copolymer can be optimized for inclusion in specific vehicles. For example, polymers which are soluble in an aqueous formulation preferably have the composition: from 0% to 70% (preferably from 5% to 70% monomer A, from 30% to 98% (preferably from 30% to 80% monomer B, and from 1% to 40% monomer C. Polymers which are dispersible have the preferred composition: from 0% to 70% (more preferably from 5% to 70%) monomer A, from 20% to 80% (more preferably from 20% to 60%) monomer B, and from 1% to 40% monomer C.

In one aspect of the present invention, the polymers comprise from 5% to 98% A monomer, from 0.01% to 50% C monomer, and from 0% to 98% B monomer. In these polymers, it is preferred that A be selected from t-butylacrylate, t-butylimethacrylate, and mixtures thereof, since such polymers can be dissolved directly in cyclomethicone solvents without requiring co-solvents. This is surprising in view of US-A-4,693,935 (Mazurek) and US-A-4,728,571 (Clemens et al.) which suggest that tertiary alcohols are not suitable A monomers.

Particularly preferred polymers for use in the present invention include the following (the weight percents below refer to the amount of reactants added in the polymerization reaction, not necessarily the amount in the finished polymer):

acrylic acid/n-butylmethacrylate/(polydimethylsiloxane (PDMS) macromer-20,000 molecular weight) (10/70/20 w/w/w) (I)

N,N-dimethylacrylamide/isobutyl methacrylate/(PDMS macromer - 20,000 molecular weight) (20/60/20 w/w/w) (II)

dimethylaminoethyl methacrylate/isobutyl methacrylate/2-ethylhexylmethacrylate/(PDMS macromer-20,000 molecular weight) (25/40/15/20 w/w/w/w) (III)

dimethylacrylamide/(PDMS macromer - 20,000 molecular weight) (80/20 w/w) (IV)

t-butylacrylate/t-butylimethacrylate/(PDMS macromer - 10,000 molecular weight) (56/24/20 w/w/w) (V)

t-butylacrylate/(PDMS macromer - 10,000 molecular weight) (80/20 w/w) (VI)

t-butylacrylate/N,N-dimethylacrylamide/(PDMS macromer 10,000 molecular weight) (70/10/20) (VII)

t-butylacrylate/acrylic acid/(PDMS macromer - 10,000 molecular weight) (75/5/20) (VIII)

The silicone-containing copolymers described above are synthesized as follows.

The polymers are synthesized by free radical polymerization methods, the general principles of which are well understood. See, for example, Odian, "Principles of Polymerization", 2nd edition, John Wiley & Sons, 1981, pp. 179-318. The desired monomers are all placed in a reactor, along with a sufficient amount of a mutual solvent so that when the reaction is complete the viscosity of the reaction is reasonable. Typical monomer loadings are from 20% to 50%. Undesired terminators, especially oxygen, are removed as needed. This is done by evacuation or by purging with an inert gas, such as argon or nitrogen. The initiator is introduced and the reaction brought to the temperature needed for initiation to occur, assuming thermal initiators are used. Alternatively, redox or radiation initiation can be used as desired. The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved, typically from a few hours to a few days. The solvent is then removed, usually by evaporation or by precipitating the polymer by addition of a nonsolvent. The polymer is further purified as needed.

By way of example, Polymers I, II and III, described above, are synthesized in the following manner. There are numerous variations on these procedures which are entirely up to the discretion of the synthetic chemist (e.g., choice of degassing method and gas, choice of initiator type, extent of conversion, reaction loading, etc). The choice of initiator and solvent are often determined by the requirements of the particular monomers used, since different monomers have different solubilities and different reactivities to a specific initiator.

Polymer I: Place 10 parts acrylic acid, 70 parts n-butyl-methacrylate, and 20 parts 20K PDMS macromer in a flask. Add sufficient ethyl acetate to produce a final monomer concentration of 40%. Add initiator, benzoyl

peroxide, to a level of 0.5% by weight relative to the amount of monomer. Evacuate the vessel, and refill with nitrogen. Heat to 60°C and maintain this temperature for 48 hours while agitating. Terminate the reaction by cooling to room temperature, and dry off the ethyl acetate by pouring the reaction mixture into a teflon (RTM) coated pan and placing in a vacuum oven.

Polymer II: Place 20 parts N,N-dimethylacrylamide, 60 parts isobutylmethacrylate, and 20 parts silicone macromer in a reaction vessel fitted with a temperature probe, reflux condenser, inlet port, and argon sparge. Add sufficient toluene to bring the final monomer concentration to 20% by weight. Sparge with argon for 1 to 2 hours. While sparging, heat to 62°C, with a sufficient rate of argon flow to keep the solution mixed. Add initiator, azobisisobutyronitrile, to a level of 0.25% by weight relative to the weight of monomer present. Monitor the reaction visually, ensuring that no phase separation of reactants occurs during polymerization. If any turbidity is observed, add sufficient warm degassed toluene to eliminate the turbidity. Continue to monitor throughout the reaction. Terminate the reaction after 4 to 6 hours and purify as with Polymer I.

Polymer III: Place 25 parts dimethylaminoethylmethacrylate, 15 parts 2-ethylhexylmethacrylate, 40 parts isobutylmethacrylate, and 20 parts 20K PDMS macromer in a reaction vessel fitted with a mechanical stirrer, argon sparge, temperature probe, reflux condenser and inlet port. Add sufficient toluene to bring the final monomer concentration to 30% by weight. Begin stirring and sparge with argon for 2 hours. While sparging, heat to 60°C in a water bath. Add initiator, azobisisobutyronitrile, to a level of 0.15% by weight relative to the weight of monomer present. Continue stirring and a slow argon sparge and maintain the reaction temperature at 60°C. Allow to react for 24 hours. Terminate the reaction and remove the solvent as with Polymer I.

#### Carrier

The compositions of the invention also comprise a carrier, or a mixture of such carriers, which are suitable for application to hair. The carriers are present at from 0.5% to 99.5%, preferably from 5.0% to 99.5%, most preferably from 10.0% to 90.0%, of the composition. As used herein, the phrase "suitable for application to hair" means that the carrier does not damage or negatively affect the aesthetics of hair or cause irritation to skin. Choice of appropriate carrier will also depend on the particular copolymer to be used, and whether the product formulated is meant to be left on hair (e.g., hair spray, mousse, tonic) or rinsed off (e.g., shampoo, conditioner) after use.

The carriers used herein include solvents, as well as other carrier or vehicle components conventionally used in hair care compositions. The solvent selected must be able to dissolve or disperse the particular silicone copolymer being used. The nature and proportion of B monomer in the copolymer largely determines its polarity and solubility characteristics. The silicone copolymers can be designed, by appropriate combination of monomers, for formulation with a wide range of solvents. Suitable solvents for use in the present invention include, but are not limited to, water, lower alcohols (such as ethanol, isopropanol), hydroalcoholic mixtures, hydrocarbons (such as isobutane, hexane, decene, acetone), halogenated hydrocarbons (such as Freon RTM), linalool, hydrocarbon esters (such as ethyl acetate, dibutyl phthalate), volatile silicon derivatives, especially siloxanes (such as phenyl pentamethyl disiloxane, methoxypropyl heptamethyl cyclotetrasiloxane, chloropropyl pentamethyl disiloxane, hydroxypropyl pentamethyl disiloxane, octamethyl cyclotetrasiloxane, decamethyl cyclopentasiloxane), and mixtures thereof. Preferred solvents include water, ethanol, volatile silicon derivatives, and mixtures thereof. The solvents used in such mixtures may be miscible or immiscible with each other.

Where the hair care compositions are conditioner compositions, the carrier may include gel vehicle materials. This gel vehicle comprises two essential components: a lipid vehicle material and a cationic surfactant vehicle material. Cationic surfactant materials are described in detail below. Gel-type vehicles are generally described in the following documents, Barry, "The Self Bodying Action of the Mixed Emulsifier Sodium Dodecyl Sulfate/Cetyl Alcohol", 28 *J. of Colloid and Interface Science* 82-91 (1968); Barry, et al., "The Self-Bodying Action of Alkyltrimethylammonium Bromides/Cetostearyl Alcohol Mixed Emulsifiers; Influence of Quaternary Chain Length", 35 *J. of Colloid and Interface Science* 689-708 (1971); and Barry, et al., "Rheology of Systems Containing Cetomacrogol 1000 - Cetostearyl Alcohol, I. Self Bodying Action", 38 *J. of Colloid and Interface Science* 616-625 (1972).

The vehicles may incorporate one or more lipid vehicle materials which are essentially water-insoluble, and contain hydrophobic and hydrophilic moieties. Lipid vehicle materials include naturally or synthetically-derived acids, acid derivatives, alcohols, esters, ethers, ketones, and amides with carbon chains of from 12 to 22, preferably from 16 to 18, carbon atoms in length. Fatty alcohols and fatty esters are preferred; fatty alcohols are particularly preferred.

Lipid vehicle materials among those useful herein are disclosed in Bailey's Industrial Oil and Fat Products, (3rd edition, D. Swern, ed., 1979), Fatty alcohols included among those useful herein are disclosed in the following documents, US-A-3,155,591, Häfner, issued November 3, 1964; US-A-4,165,369, Watanabe, et al., is-

sued August 21, 1979; US-A-4,269,824, Villamarin, et al., issued May 26, 1981; BP-A 1,532,585, published November 15, 1978; and Fukushima, et al., "The Effect of Cetostearyl Alcohol in Cosmetic Emulsions", 98 *Cosmetics & Toiletries* 89-112 (1983). Fatty esters included among those useful herein are disclosed in US-A 3,341,465, Kaufman, et al., issued September 12, 1976. If included in the compositions of the present invention, the lipid vehicle material is present at from 0.1% to 10.0% of the composition; the cationic surfactant vehicle material is present at from 0.5% to 5.0% of the composition.

Preferred esters for use herein include cetyl palmitate and glycerylmonostearate. Cetyl alcohol and stearyl alcohol are preferred alcohols. A particularly preferred lipid vehicle material is comprised of a mixture of cetyl alcohol and stearyl alcohol containing from 55% to 65% (by weight of mixture) of cetyl alcohol.

Preferred vehicles for use in the compositions of the present invention include combinations of hydrophobically-modified hydroxyethyl cellulose materials with thickeners (such as locust bean gum), particular surfactants, quaternary ammonium compounds (such as ditallowdimethyl ammonium chloride), and/or chelating agents (such as EDTA).

Other carriers, suitable for use with the present invention are, for example, those used in the formulation of tonics, mousses, gels and hair sprays. Tonics, gels and non-aerosol hair sprays utilize a solvent such as water or alcohol while mousses and aerosol hair sprays additionally utilize a propellant such as trichlorofluoromethane, dichlorodifluoromethane, dimethylether, propane, n-butane or isobutane. A tonic or hair spray product having a low viscosity may also require an emulsifying agent to keep the silicone copolymer homogeneously dispersed in solution. Examples of suitable emulsifying agents include nonionic, cationic, anionic surfactants, or mixtures thereof. If such an emulsifying agent is used, it is present at a level of from 0.25% to 7.5% of the composition. The level of propellant can be adjusted as desired but is generally from 3% to 30% of mousse compositions and from 15% to 50% of the aerosol hair spray compositions.

#### Optional Ingredients

The hair care compositions of the present invention may be formulated in a wide variety of product types, including mousses, gels, lotions, tonics, sprays, shampoos and conditioners. The additional components required to formulate such products vary with product type and can be routinely chosen by one skilled in the hair care product art. The following is a description of some of these additional components.

#### Surfactants

Surfactants are preferred optional ingredients in the compositions of the invention, particularly shampoo and conditioner compositions. When present, the surfactant comprises from 0.05% to 50% of the composition. For a shampoo, the level is preferably from 10% to 30%, most preferably from 12% to 25%, of the composition. For conditioners, the preferred level of surfactant is from 0.2% to 3%. Surfactants useful in compositions of the present invention include anionic, nonionic, cationic, zwitterionic and amphoteric surfactants.

Synthetic anionic detergents useful herein, particularly for shampoo compositions, include alkyl and alkyl ether sulfates. These materials have the respective formulae  $\text{ROSO}_3\text{M}$  and  $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$ , wherein R is alkyl or alkenyl of from 10 to 20 carbon atoms, x is 1 to 10, and M is a water-soluble cation such as ammonium, sodium, potassium and triethanolamine. The alkyl ether sulfates useful in the present invention are condensation products of ethylene oxide and monohydric alcohols having from 10 to 20 carbon atoms. Preferably, R has from 12 to 18 carbon atoms in both the alkyl and alkyl ether sulfates. The alcohols can be derived from fats, e.g., coconut oil or tallow, or can be synthetic. Lauryl alcohol and straight chain alcohols derived from coconut oil are preferred herein. Such alcohols are reacted with 1 to 10, and especially 3, molar proportions of ethylene oxide and the resulting mixture of molecular species, having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

Specific examples of alkyl ether sulfates which may be used in the present invention are sodium coconut alkyl triethylene glycol ether sulfate; sodium tallow alkyl triethylene glycol ether sulfate; and sodium tallow alkyl hexaoxyethylene sulfate. Highly preferred alkyl ether sulfates are those comprising a mixture of individual compounds, said mixture having an average alkyl chain length of from 12 to 16 carbon atoms and an average degree of ethoxylation of from 1 to 4 moles of ethylene oxide. Such a mixture also comprises from 0 to 20% by weight  $\text{C}_{12-13}$  compounds; from 60 to 100% by weight of  $\text{C}_{14-15-16}$  compounds, from 0 to 20% by weight of  $\text{C}_{17-18-19}$  compounds; from 3 to 30% by weight of compounds having a degree of ethoxylation of 0; from 45 to 90% by weight of compounds having a degree of ethoxylation of from 1 to 4; from 10 to 25% by weight of compounds having a degree of ethoxylation of from 4 to 8; and from 0.1 to 15% by weight of compounds having a degree of ethoxylation greater than 8.



Another suitable class of anionic surfactants are the water-soluble salts of the organic, sulfuric acid reaction products of the general formula:



5 wherein  $R_1$  is chosen from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from 8 to 24, preferably 12 to 18, carbon atoms; and M is a cation. Important examples are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, ineso-, and n-paraffins, having 8 to 24 carbon atoms, preferably 12 to 18 carbon atoms and a sulfonating agent, e.g.,  $SO_3$ ,  $H_2SO_4$ , oleum, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated  $C_{12-18}$  n-paraffins.

Additional examples of anionic synthetic surfactants which come within the terms of the present invention are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other anionic synthetic surfactants of this variety are set forth in US-A 2,486,921; US-A 2,486,922; and US-A 2,396,278.

Still other anionic synthetic surfactants include the class designated as succinamates. This class includes such surface active agents as disodium N-octadecylsulfosuccinamate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinamate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl esters of sodium sulfosuccinic acid.

20 Other suitable anionic surfactants utilizable herein are olefin sulfonates having 12 to 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of  $\alpha$ -olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid  $SO_2$ , chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous  $SO_2$ , etc., when used in the gaseous form.

The  $\alpha$ -olefins from which the olefin sulfonates are derived are mono-olefins having 12 to 24 carbon atoms, preferably 14 to 16 carbon atoms. Preferably, they are straight chain olefins. Examples of suitable 1-olefins include 1-dodecene; 1-tetradecene; 1-hexadecene; 1-octadecene; 1-eicosene and 1-tetracosene.

30 In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process.

A specific  $\alpha$ -olefin sulfonate mixture of the above type is described more fully in the US-A-3,332,880, Pflaumer and Kessler, issued July 25, 1967,.

Another class of anionic organic surfactants are the  $\beta$ -alkyloxy alkane sulfonates. These compounds have the following formula:



where  $R_1$  is a straight chain alkyl group having from 6 to 20 carbon atoms,  $R_2$  is a lower alkyl group having from 1 (preferred) to 3 carbon atoms, and M is a water-soluble cation as hereinbefore described.

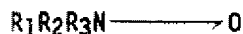
50 Specific examples of  $\beta$ -alkyloxy-alkane-1-sulfonates, or alternatively 2-alkyloxy-alkane-1-sulfonates, having low hardness (calcium ion) sensitivity useful herein include: potassium- $\beta$ -methoxydecane-sulfonate, sodium 2-methoxy-tridecane-sulfonate, potassium 2-ethoxytetradecylsulfonate, sodium 2-isopropoxyhexadecylsulfonate, lithium 2-t-butoxytetradecylsulfonate, sodium  $\beta$ -methoxyoctadecylsulfonate, and ammonium  $\beta$ -n-propoxydodecylsulfonate.

Many additional nonsoap synthetic anionic surfactants are described in McCutcheon's Detergents and Emulsifiers, 1984, Annual, published by Allured Publishing Corporation. Also US-A-3,929,678, Laughlin et al., issued December 30, 1975, discloses many other anionic as well as other surfactant types.

Nonionic surfactants, which are preferably used in combination with an anionic, amphoteric or zwitterionic surfactant, can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hy-

drophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. Examples of preferred classes of nonionic surfactants are:

1. The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to from 10 to 60 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane, or nonane, for example.
2. Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products which may be varied in composition depending upon the balance between the hydrophobic and hydrophilic elements which is desired. For example, compounds containing from 40% to 80% polyoxyethylene by weight and having a molecular weight of from 5,000 to 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2,500 to 3,000, are satisfactory.
3. The condensation product of aliphatic alcohols having from 8 to 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from 10 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms.
4. Long chain tertiary amine oxides corresponding to the following general formula:



wherein  $R_1$  contains an alkyl, alkenyl or monohydroxy alkyl radical of from 8 to about 18 carbon atoms, from 0 to 10 ethylene oxide moieties, and from 0 to 1 glyceryl moiety, and  $R_2$  and  $R_3$  contain from 1 to 3 carbon atoms and from 0 to 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals. The arrow in the formula is a conventional representation of a semipolar bond. Examples of amine oxides suitable for use in this invention include dimethyl-dodecylamine oxide, oleyldi(2-hydroxyethyl) amine oxide, dimethyloctylamine oxide, dimethyl-decylamine oxide, dimethyl-tetradecylamine oxide, 3,6,9-trioxaheptadecyldiethylamine oxide, di(2-hydroxyethyl)-tetradecylamine oxide, 2-dodecoxyethyl-dimethylamine oxide, 3-dodecoxy-2-hydroxypropyldi(3-hydroxypropyl)amine oxide, dimethylhexadecylamine oxide.

5. Long chain tertiary phosphine oxides corresponding to the following general formula:



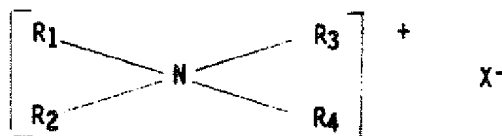
wherein  $R$  contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from 8 to 18 carbon atoms in chain length, from 0 to 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety and  $R'$  and  $R''$  are each alkyl or monohydroxyalkyl groups containing from 1 to 3 carbon atoms. The arrow in the formula is a conventional representation of a semipolar bond. Examples of suitable phosphine oxides are: dodecyldimethylphosphine oxide, tetradecyldimethylphosphine oxide, tetradecylmethylethylphosphine oxide, 3,6,9-trioxa-octadecyldimethylphosphine oxide, cetyldimethylphosphine oxide, 3-dodecoxy-2-hydroxypropyldi(2-hydroxyethyl) phosphine oxide, stearyldimethylphosphine oxide, cetylethylpropylphosphine oxide, oleyldiethylphosphine oxide, dodecyldiethylphosphine oxide, tetradecyldiethylphosphine oxide, dodecyldipropylphosphine oxide, dodecyldi(hydroxymethyl)phosphine oxide, dodecyldi(2-hydroxyethyl)phosphine oxide, tetradecylmethyl-2-hydroxypropylphosphine oxide, oleyldimethylphosphine oxide, 2-hydroxydodecyldimethylphosphine oxide.

6. Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from 1 to 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from 8 to 20 carbon atoms, from 0 to 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety. Examples include: octadecyl methyl sulfoxide, 2-ketotridecyl methyl sulfoxide, 3,6,9-trioxa-octadecyl 2-hydroxyethyl sulfoxide, dodecyl methyl sulfoxide, oleyl 3-hydroxypropyl sulfoxide, tetradecyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

Cationic surfactants useful in compositions of the present invention, particularly the conditioner compositions, contain amino or quaternary ammonium hydrophilic moieties which are positively charged when dissolved in the aqueous composition of the present invention. Cationic surfactants among those useful herein are disclosed in the following documents, M.C. Publishing Co., McCutcheon's, Detergents & Emulsifiers, (North American edition 1979); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New

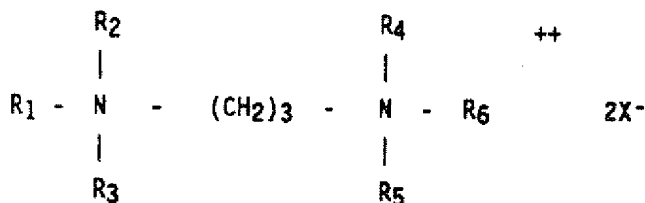
York: Interscience Publishers, 1949; US-A-3,155,591, Hilfer, issued November 3, 1964; US-A-3,929,678, Laughlin, et al., issued December 30, 1975; US-A-3,959,461, Bailey, et al., issued May 25, 1976; and US-A-4,387,090, Bolich, Jr., issued June 7, 1983. If included in the compositions of the present invention, the cationic surfactant is present at from 0.05% to 5%.

Among the quaternary ammonium-containing cationic surfactant materials useful herein are those of the general formula:



wherein  $R_1 - R_4$  are independently an aliphatic group of from 1 to 22 carbon atoms, or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having from 12 to 22 carbon atoms; and  $X$  is an anion selected from halogen, acetate, phosphate, nitrate and alkylsulfate radicals. The aliphatic groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups.

Other quaternary ammonium salts useful herein have the formula:



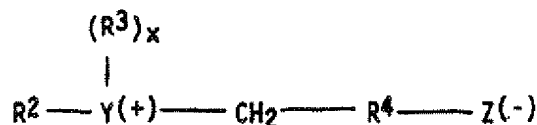
wherein  $R_1$  is an aliphatic group having from 16 to 22 carbon atoms,  $R_2, R_3, R_4, R_5$ , and  $R_6$  are selected from hydrogen and alkyl having from about 1 to about 4 carbon atoms, and  $X$  is an ion selected from halogen, acetate, phosphate, nitrate and alkyl sulfate radicals. Such quaternary ammonium salts include tallow propane diammonium dichloride.

Preferred quaternary ammonium salts include dialkyldimethylammonium chlorides, wherein the alkyl groups have from 12 to 22 carbon atoms and are derived from long-chain fatty acids, such as hydrogenated tallow fatty acid (tallow fatty acids yield quaternary compounds wherein  $R_1$  and  $R_2$  have predominately from 16 to 18 carbon atoms). Examples of quaternary ammonium salts useful in the present invention include ditallowdimethyl ammonium chloride, ditallowdimethyl ammonium methyl sulfate, dihexadecyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium chloride, dioctadecyl dimethyl ammonium chloride, dilauryl dimethyl ammonium chloride, didocosyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium acetate, dihexadecyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium acetate, ditallow dipropyl ammonium phosphate, ditallow dimethyl ammonium nitrate, di(coconutalkyl) dimethyl ammonium chloride, and stearyl dimethyl benzyl ammonium chloride. Ditallow dimethyl ammonium chloride, dicetyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride and cetyl trimethyl ammonium chloride are preferred quaternary ammonium salts useful herein. Di-(hydrogenated tallow) dimethyl ammonium chloride is a particularly preferred quaternary ammonium salt.

Salts of primary, secondary and tertiary fatty amines are also preferred cationic surfactant materials. The alkyl groups of such amines preferably have from 12 to 22 carbon atoms, and may be substituted or unsubstituted. Secondary and tertiary amines are preferred, tertiary amines are particularly preferred. Such amines, useful herein, include stearamido propyl dimethyl amine, diethyl amino ethyl stearamide, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated (5 moles E.O.) stearylamine, dihydroxy ethyl stearylamine, and arachidylbehenylamine. Suitable amine salts include the halogen, acetate, phosphate, nitrate, citrate, lactate and alkyl sulfate salts. Such salts include stearylamine hydrochloride, soyamine chloride, stearylamine formate, N-tallowpropane diamine dichloride and stearamidopropyl dimethylamine citrate. Cationic amine surfactants included among those useful in the present invention are disclosed in US-A-4,275,055, Nachtigai, et al., issued June 23, 1981.

Zwitterionic surfactants, useful in shampoos as well as conditioners, are exemplified by those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., car-

boxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



wherein  $R^2$  contains an alkyl, alkenyl, or hydroxy alkyl radical of from 8 to 18 carbon atoms, from 0 to 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety;  $Y$  is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms;  $R^3$  is an alkyl or monohydroxyalkyl group containing 1 to 3 carbon atoms;  $X$  is 1 when  $Y$  is a sulfur atom, and 2 when  $Y$  is a nitrogen or phosphorus atom;  $R^4$  is an alkylene or hydroxyalkylene of from 1 to 4 carbon atoms and  $Z$  is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Examples of such surfactants include:

- 4-[N,N-di(2-hydroxyethyl)-N-octadecylammonio]-butane-1-carboxylate;
- 5-[S-3-hydroxypropyl-S-hexadecylsulfonio]-3-hydroxypentane-1-sulfate;
- 3-[P,P-diethyl-P-3,6,9-trioxatetradecoxylphosphonio]-2-hydroxy-propane-1-phosphate;
- 3-[N,N-dipropyl-N-3-dodecoxy-2-hydroxypropylammonio]-propane-1-phosphonate;
- 3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate;
- 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate;
- 4-[N,N-di(2-hydroxyethyl)-N-(2-hydroxydodecyl)ammonio]-butane-1-carboxylate;
- 3-[S-ethyl-S-(3-dodecoxy-2-hydroxypropyl)sulfonio]-propane-1-phosphate;
- 3-[P,P-dimethyl-P-dodecylphosphonio]-propane-1-phosphonate; and
- 5-[N,N-di(3-hydroxypropyl)-N-hexadecylammonio]-2-hydroxy-pentane-1-sulfate.

Other zwitterionics such as betaines are also useful in the present invention. Examples of betaines useful herein include the high alkyl betaines, such as coco dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alphacarboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl bis-(2-hydroxyethyl) carboxymethyl betaine, stearyl bis-(2-hydroxypropyl) carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, and lauryl bis-(2-hydroxypropyl)alpha-carboxyethyl betaine. The sulfobetaines may be represented by coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxyethyl) sulfopropyl betaine and the like; amidobetaines and amidosulfobetaines, wherein the  $RCONH(CH_2)_3$  radical is attached to the nitrogen atom of the betaine are also useful in this invention.

Examples of amphoteric surfactants which can be used in the compositions of the present invention are those which are broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecyl-aminopropionate, sodium 3-dodecylaminopropane sulfonate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of US-A-2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of US-A-2,438,091, and the products sold under the trade name "Miranol" (RTM) and described in US-A-2,528,378.

The above-mentioned surfactants can be used alone or in combination in the hair care compositions of the present invention. The alkyl sulfates, ethoxylated alkyl sulfates and mixtures thereof are preferred for use herein.

The hair care compositions herein can contain a variety of other optional components suitable for rendering such compositions more cosmetically or aesthetically acceptable or to provide them with additional usage benefits. Such conventional optional ingredients are well-known to those skilled in the art, e.g., pearlescent aids, such as ethylene glycol distearate; preservatives, such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; thickeners and viscosity modifiers, such as a diethanolamide of a long chain fatty acid (e.g., PEG 3 lauric diethanolamide), cocomonooethanol amide, dimethicone copolyols, guar gum, methyl cellulose, starches and starch derivatives; fatty alcohols, such as cetearyl alcohol; sodium chloride; sodium sulfate; polyvinyl alcohol; ethyl alcohol; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, and sodium carbonate; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents, such as the thioglycolates; perfumes; sequestering agents, such as disodium ethylenediamine tetra-acetate; and polymer plasticizing agents, such as glycerin and propylene glycol. Such optional ingredients generally

are used individually at levels of from 0.01% to 10.0%, preferably from 0.05% to 5.0%, of the composition.

The pH of the present compositions should be between 3 and 9, preferably between 4 and 8.

As with all compositions, the present invention should not contain components which unduly interfere with the performance of the compositions.

The hair care compositions of the present invention can be made using conventional formulation and mixing techniques. Methods of making various types of hair care compositions are described more specifically in the following examples.

#### Method of Use

The hair care compositions of the present invention are used in conventional ways to provide the hair conditioning/styling/hold benefits of the present invention. Such method of use depends upon the type of composition employed but generally involves application of an effective amount of the product to the hair, which may then be rinsed from the hair (as in the case of shampoos and some conditioning products) or allowed to remain on the hair (as in the case of spray, mousse, gel, and tonic products). By "effective amount" is meant an amount sufficient to provide the hair conditioning/styling/hold benefits desired considering the length and texture of the hair, and the type of product used. Preferably, the product is applied to wet or damp hair prior to drying and styling of the hair. After the compositions of the present invention are applied to the hair, the hair is dried and styled in the usual ways of the user.

The following examples further illustrate preferred embodiments within the scope of the present invention.

The following table defines the silicone copolymers used in the examples (weight ratios given refer to proportion added to reaction mix):

Copolymer #1	10/70/20 acrylic acid/n-butylmethacrylate/silicone macromer S2, polymer molecular weight about 100,000
Copolymer #2	10/70/20 dimethylaminoethyl methacrylate/isobutyl methacrylate/silicone macromer S2, polymer molecular weight about 400,000
Copolymer #3	60/20/20 quaternized dimethylaminoethyl methacrylate/isobutyl methacrylate/silicone macromer S1, polymer molecular weight about 500,000
Copolymer #4	40/40/20 acrylic acid/methyl methacrylate/silicone macromer S1, polymer molecular weight about 400,000
Copolymer #5	10/70/20 acrylic acid/n-butyl methacrylate/silicone macromer S1, polymer molecular weight about 300,000
Copolymer #6	25/65/10 acrylic acid/isopropyl methacrylate/silicone macromer S2, polymer molecular weight about 200,000
Copolymer #7	60/25/15 N,N-dimethylacrylamide/methoxyethyl methacrylate/silicone macromer S1, polymer molecular weight about 200,000
Copolymer #8	12/64/4/20 N,N-dimethylacrylamide/isobutyl methacrylate/2-ethylhexyl methacrylate/PDMS macromer S1, polymer molecular weight about 300,000
Copolymer #9	30/40/10/20 dimethylaminoethyl methacrylate/isobutyl methacrylate/2-ethylhexyl methacrylate/PDMS macromer S1, polymer molecular weight about 300,000
Copolymer #10	80/20 t-butylacrylate/PDMS macromer S2, polymer molecular weight about 150,000

Silicone macromer S1- has a molecular weight of 20,000 and is prepared in a manner similar to Example C-2c of US-A-4,728,571, Clemens, issued March 1, 1988.

Silicone macromer S2- has a molecular weight of 10,000 and is prepared in a manner similar to Example C-2b of US-A-4,728,571, Clemens, issued March 1, 1988.

#### EXAMPLE I

The following is a hair spray composition representative of the present invention.

<u>Component</u>	<u>Weight %</u>
Silicone Copolymer #4	2.00
Ethanol	72.90
Perfume	0.10
Isobutane propellant	25.00

This product is prepared by adding the silicone copolymer and perfume to the ethanol and mixing for several hours until all the polymer is dissolved. This "concentrate" is then placed in aerosol cans which are fitted with valves crimped under vacuum and then filled through the valve stem with isobutane dispensed by a pressure filler.

#### EXAMPLE II

The following is a shampoo composition representative of the present invention.

<u>Component</u>	<u>Weight %</u>
<u>Styling Agent</u>	
Silicone Copolymer #2	1.00
Chlorpropyl heptamethyl cyclotetrasiloxane	3.00
<u>Premix</u>	
Silicone gum	0.50
Dimethicone, 350 cs. fluid	0.50
<u>Main Mix</u>	
Ammonium lauryl sulfate	11.00
Cocamide MEA	2.00
Ethylene glycol distearate	1.00
Xanthan gum	1.20
Kathon (RTM) CG <sup>1</sup>	0.04
Citric acid to pH 4.5	q.s.
Double reverse osmosis (DRO) H <sub>2</sub> O	q.s.
<sup>1</sup> preservative commercially available from Rohm & Haas	

The Styling Agent and Premix are blended separately in a conventional manner. The Main Mix is prepared by first dissolving the xanthan gum in the water with conventional mixing. The remaining Main Mix ingredients are added and the Main Mix is heated to 150°F with agitation for 1/2 hour. The Styling Agent and Premix are then added sequentially with ten minutes agitation between additions, and the entire mixture is stirred while the batch is cooled to room temperature. For varied particle size, the Styling Agent and Premix can be added at different times using either or both high shear mixing (high speed dispersator) or normal agitation.

#### EXAMPLE III

The following is a shampoo composition representative of the present invention.

<u>Component</u>	<u>Weight %</u>
Ammonium lauryl sulfate	7.00
Ammonium laureth sulfate	7.00
Cocamide MEA	2.50
Silicone Copolymer #3	1.00
Natrosol (RTM) 250H <sup>1</sup>	1.00
Glydant <sup>2</sup> (RTM)	0.37
DRO H <sub>2</sub> O	q.s.
<sup>1</sup> hydroxyethyl cellulose commercially available from Aqualon Co.	
<sup>2</sup> preservative commercially available from Glyco, Inc.	

The shampoo is made by first dispersing the Natrosol (RTM) and silicone copolymer in the water for 1 hour with conventional agitation. The remaining ingredients are then added.

#### EXAMPLE IV

The following is a styling rinse composition representative of the present invention.

<u>Component</u>	<u>Weight %</u>
<u>Styling Agent Premix</u>	
Silicone Copolymer #8	2.00
Phenethylpentamethyl disiloxane	6.00

	Octamethyl cyclotetrasiloxane	3.00
	<u>Xanthan Premix</u>	
5	Xanthan gum	0.25
	DRO H <sub>2</sub> O	25.00
	<u>Main Mix</u>	
10	Dihydrogenated tallow-dimethylammonium chloride (DTDMAC)	0.50
	EDTA, disodium salt	0.10
15	D.C. (RTM) 929 <sup>1</sup>	2.00
	Perfume	0.10
	Poly Surf (RTM) C <sup>2</sup>	0.75
	Locust bean gum	0.75
20	Kathon (RTM) CG <sup>3</sup>	0.04
	DRO H <sub>2</sub> O	q.s.
	<sup>1</sup> amodimethicone, commercially available from Dow Corning	
25	<sup>2</sup> hydrophobically- modified hydroxyethyl cellulose, commercially available from Aqualon Co.	
	<sup>3</sup> preservative commercially available from Rohm and Haas	

30 The Styling Agent and Xanthan Premixes are blended separately in a conventional manner. The Main Mix is prepared by adding all the ingredients together and heating with agitation to 95°C for 1/2 hour. As the batch is cooled, the Styling Agent and Xanthan Premixes are added at about 80°C with vigorous mixing. The batch is then cooled to ambient temperature.

#### 35 EXAMPLE V

The following is a styling rinse composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
40	<u>Premix A</u>	
	Silicone Copolymer #3	2.00
	DRO H <sub>2</sub> O	10.00
45	<u>Premix B</u>	
	Silicone Copolymer #4	2.00
	DRO H <sub>2</sub> O	15.00
50	NaOH solution (50%)	0.20
	<u>Main Mix</u>	
	Poly Surf (RTM) C <sup>1</sup>	1.00

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	Stearamide DEA	0.50
	Ethanol	10.00
5	Perfume	0.20
	DRO H <sub>2</sub> O	q.s.
10	<sup>1</sup> hydrophobically-modified hydroxyethyl cellulose, commercially available from Aqualon Co.	

Both premixes are blended separately in a conventional manner. The Main Mix is prepared by adding all the ingredients together and heating to about 60°C with mixing. The premixes are then added to the Main Mix with agitation for 1/2 hour and the batch is cooled to ambient temperature. Either sodium hydroxide or citric acid, if necessary, is added to adjust composition pH to 6.5.

#### EXAMPLE VI

The following is a hair grooming tonic composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
	Silicone Copolymer #9	0.70
	Perfume	0.10
25	Ethanol	q.s.

The composition is made by mixing the above components together in a conventional manner.

#### EXAMPLE VII

The following is a shampoo composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
35	Ammonium laureth sulfate	7.00
	Cocamido propyl betaine	6.00
	Silicone Copolymer #6	2.00
40	Ethanol	10.00
	PEG 150 distearate	2.00
	Glydant (RTM) <sup>1</sup>	0.38
45	Perfume	1.00
	DRO H <sub>2</sub> O	q.s.

<sup>1</sup> preservative commercially available from Glyco, Inc.

The shampoo is prepared by combining the ammonium laureth sulfate (normally supplied as a 28% solution in water) and Silicone Copolymer and heating to 70°C for 1/2 hour with mixing. The remaining ingredients are added and mixed for an additional 1/2 hour. The batch is then cooled to ambient temperature. Composition pH is adjusted to 6.5 by the addition of citric acid or sodium hydroxide, if necessary.

#### EXAMPLE VIII

The following is a styling rinse composition representative of the present invention.

<u>Component</u>	<u>Weight %</u>
<u>Styling Agent</u>	
Silicone Copolymer #5	3.00
Phenylpentamethyl disiloxane	9.00
<u>Premix</u>	
Silicone Gum GE (RTM) SE76 <sup>1</sup>	0.50
Decamethyl cyclopentasiloxane	4.00
<u>Main Mix</u>	
Poly Surf (RTM) C <sup>2</sup>	0.60
Locust bean gum	0.50
EDTA, disodium salt	0.15
DTDMAC	0.65
Glydant <sup>3</sup>	0.40
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> Commercially available from General Electric

<sup>2</sup> hydrophobically-modified hydroxyethyl cellulose commercially available from Aqualon Co.

<sup>3</sup> preservative commercially available from Glyco, Inc.

The Styling Agent and Premix are blended separately by conventional means. The Main Mix is prepared by adding all the ingredients and heating to 95°C for 1/2 hour with agitation. As the batch is cooled to 60°C, the Premix and Styling Agent mixes are added to the Main Mix with agitation and the batch is cooled to ambient temperature.

#### EXAMPLE IX

The following is a styling rinse composition representative of the present invention.

<u>Component</u>	<u>Weight %</u>
<u>Styling Agent</u>	

	Silicone Copolymer #10	3.00
5	Octamethyl cyclotetrasiloxane	9.00
	<u>Premix</u>	
	Silicone Gum (RTM) GE SE76 <sup>1</sup>	0.50
	Decamethyl cyclopentasiloxane	4.00
10	<u>Main Mix</u>	
	Poly Surf C (RTM) <sup>2</sup>	1.25
	Stearamide DEA	0.40
15	DTDMAC	0.50
	Kathon (RTM) CG <sup>3</sup>	0.03
	Imidazole	0.15
	Perfume	0.10
20	DRO H <sub>2</sub> O	q.s.
	<sup>1</sup> Commercially available from General Electric	
	<sup>2</sup> hydrophobically-modified hydroxyethyl cellulose commercially	
25	available from Aqualon Co.	
	<sup>3</sup> preservative commercially available from Rohm & Haas	

30 The Styling Agent and Premix are blended separately by conventional means. The Main Mix is prepared by adding all the ingredients and heating to 95°C for 1/2 hour with agitation. As the batch is cooled to 60°C, the Premix and Styling Agent mixes are added to the Main Mix with agitation and the batch is cooled to ambient temperature.

#### 35 EXAMPLE X

The following is a cold-wave hair perm composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
40	Thioglycolic acid	5.00
	Monoethanolamine	6.00
	Silicone Copolymer #3	1.50
45	PEG 10 monostearate	0.50
	DRO H <sub>2</sub> O	q.s.

The composition is prepared by blending all the ingredients with agitation for 1/2 hour at 60°C and then cooling to ambient temperature.

#### 50 EXAMPLE XI

The following is a hair conditioner composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
5	<u>Styling Agent Premix</u>	
	Silicone Copolymer #9	1.00
	Phenyl pentamethyl disiloxane	4.00
	<u>Silicone Premix</u>	
10	Silicone gum, GE SE76 <sup>1</sup> (RTM)	0.30
	Octamethyl cyclotetrasiloxane	1.70
	<u>Main Mix</u>	
15	Cetyl alcohol	1.00
	Quaternium 18 <sup>2</sup> (RTM)	0.85
	Stearyl alcohol	0.70
20	Natrosol 250 MBR <sup>3</sup> (RTM)	0.50
	Ceteareth-20	0.35
	Fragrance	0.20
	Dimethicone copolyol	0.20
25	Citric acid	0.13
	Methylchloroisothiazolinone, methylisothiazolinone	0.04
30	Sodium chloride	0.01
	DRO H <sub>2</sub> O	q.s.
	<sup>1</sup> Commercially available from General Electric	
35	<sup>2</sup> Ditallow quaternary ammonium compound, commercially available from Sherex	
	<sup>3</sup> hydroxyethyl cellulose material, commercially available from Aqualon Co.	

The product is prepared by comixing all the Main Mix ingredients, heating to 60°C with mixing, and colloid milling down to 45°C. At this temperature, the two premixes are added separately with moderate agitation and the batch allowed to cool to ambient temperature.

#### 45 EXAMPLE XII

The following is a styling gel composition representative of the present invention.

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<u>Component</u>	<u>Weight %</u>
Silicone Copolymer #7	2.00
Carbopol 940 <sup>1</sup> (RTM)	0.75
Triethanolamine	1.00
Dye solution	0.05
Perfume	0.10
Laureth-23	0.10
DRO H <sub>2</sub> O	q.s.
<sup>1</sup> cross-linked polyacrylic acid, commercially available from B. F. Goodrich	

This batch is made by mixing the listed components together in a conventional manner.

#### 20 EXAMPLE XIII

The following is a hair mousse composition representative of the present invention.

<u>Component</u>	<u>Weight %</u>
Silicone Copolymer #7	3.00
Ethanol	15.00
Cocamine oxide	0.60
D.C. 190 <sup>1</sup> (RTM)	0.20
Cocamide DEA	0.30
Perfume	0.10
Isobutane	7.00
DRO H <sub>2</sub> O	q.s.
<sup>1</sup> dimethicone copolyol, commercially available from Dow Corning	

40 The composition is made by blending all of the ingredients except isobutane at ambient temperature until well mixed. Aluminum aerosol cans are then filled with 95 parts of this batch, affixed with a valve which is crimped into position, and lastly pressure filled with 5 parts isobutane.

#### 45 EXAMPLE XIV

The following is a pump hair spray composition representative of the present invention.

<u>Component</u>	<u>weight %</u>
Silicone Copolymer #1	2.50
Dibutyl phthalate	0.20
Phenyldimethicone	0.30

Perfume	0.05
Aminomethyl propanol	0.20
Ethanol	q.s.

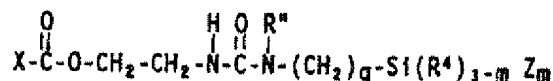
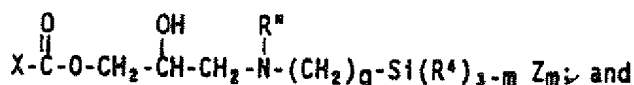
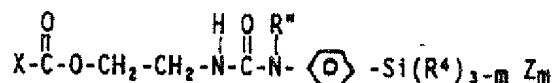
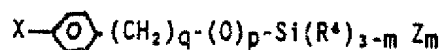
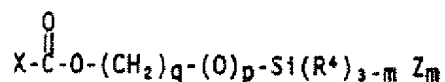
This composition is made by mixing the listed components together in a conventional manner.

When the compositions defined in Examples I-XIV are applied to hair in the conventional manner, they provide effective hair conditioning and styling/hold benefits without leaving the hair with a sticky/stiff feel.

### Claims

1. A hair care composition characterized in that it comprises:

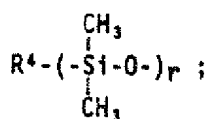
(a) from 0.1% by weight to 10.0% by weight of a silicone-containing copolymer having a molecular weight of from 10,000 to 1,000,000 comprising a component selected from: a lipophilic low polarity free radically polymerizable vinyl monomer (A), a hydrophilic polar monomer which is copolymerizable with A (B), and mixtures thereof; together with a silicone-containing macromer (C) having a weight average molecular weight of from 1,000 to 50,000 based on polydimethylsiloxane selected from



wherein m is 1, 2 or 3; p is 0 or 1; R'' is alkyl or hydrogen; q is an integer from 2 to 6; s is an integer from 0 to 2; X is

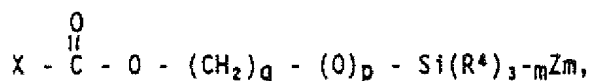


R<sup>1</sup> is hydrogen or -COOH; R<sup>2</sup> is hydrogen, methyl or -CH<sub>2</sub>COOH; Z is



R<sup>4</sup> is alkyl, alkoxy, alkylamino, aryl or hydroxyl; and r is an integer from 5 to 700;  
and wherein the silicone-containing copolymer comprises from 0% to 98% by weight monomer A, from  
0% to 98% by weight monomer B, and from 0.1% by weight to 50% by weight monomer C; and  
(b) from 0.5% by weight to 99.5% by weight of a carrier suitable for application to hair.

2. A hair care composition according to Claim 1 characterized in that the silicone-containing copolymer comprises from 5% by weight to 98% by weight monomer A, from 7.5% by weight to 80% by weight monomer B, and from 0.1% by weight to 50% by weight monomer C.
3. A hair care composition according to Claim 1 or 2 characterized in that monomer A is selected from acrylic acid esters of C<sub>1</sub>-C<sub>18</sub> alcohols, methacrylic acid esters of C<sub>1</sub>-C<sub>18</sub> alcohols, styrene, polystyrene macromer, vinyl acetate, vinyl chloride, vinyl propionate, vinylidene chloride, alpha-methylstyrene, t-butylstyrene, butadiene, cyclohexadiene, ethylene, propylene, vinyl toluene, and mixtures thereof; and is preferably selected from n-butylmethacrylate, isobutylmethacrylate, 2-ethylhexylmethacrylate, methylmethacrylate, t-butylacrylate, t-butylmethacrylate, and mixtures thereof.
4. A hair care composition according to any of Claims 1-3 characterized in that monomer B is selected from acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride, half esters of maleic anhydride, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers, maleimides, vinyl pyridine, vinyl imidazole, styrene sulfonate, allyl alcohol, vinyl alcohol, vinyl caprolactam, and mixtures thereof; and is preferably selected from acrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, and mixtures thereof.
5. A hair care composition according to any of Claims 1-4 characterized in that monomer C has the formula



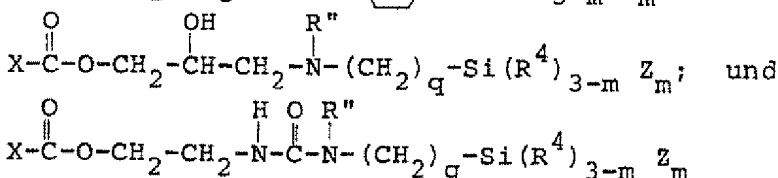
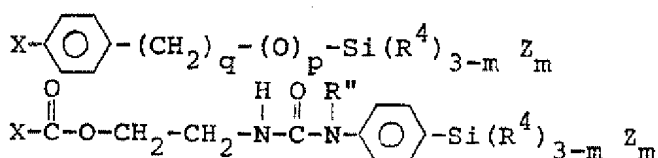
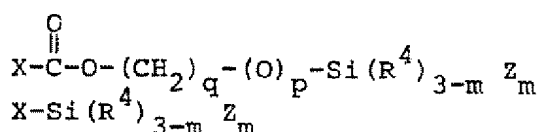
wherein p = 0 and q = 3, m is 1, r is 250, R<sup>4</sup> is alkyl, R<sup>1</sup> is hydrogen, and R<sup>2</sup> is methyl.

6. A hair care composition according to any of Claims 1-5 characterized in that the silicone-containing copolymer is selected from:  
acrylic acid/n-butylmethacrylate/polydimethylsiloxane (PDMS) macromer - 20,000 mw (10/70/20);  
N,N-dimethylacrylamide/isobutyl methacrylate/PDMS macromer 20,000 mw (20/60/20);  
dimethylaminoethyl methacrylate/isobutyl methacrylate/2-ethylhexyl methacrylate/PDMS macromer - 20,000 mw (25/40/15/20);  
dimethylaminoethyl methacrylate/isobutyl methacrylate/PDMS macromer - 20,000 mw (10/70/20);  
quaternized dimethylaminoethyl methacrylate/isobutyl methacrylate/PDMS macromer - 20,000 mw (40/40/20);  
acrylic acid/methyl methacrylate/PDMS macromer - 20,000 mw (40/40/20);  
acrylic acid/isopropyl methacrylate/PDMS macromer - 20,000 mw (25/65/10);  
N,N-dimethylacrylamide/methoxyethyl methacrylate/PDMS macromer - 20,000 mw (60/25/15);  
dimethylacrylamide/PDMS macromer - 20,000 mw (80/20);  
and mixtures thereof.
7. A hair care composition according to any of Claims 1-6 characterized in that it is in the form of a shampoo which additionally comprises from 10% by weight to 30% by weight of a synthetic surfactant, which is preferably selected from alkyl sulfates, ethoxylated alkyl sulfates, and mixtures thereof.

8. A hair care composition according to any of Claims 1-6 characterized in that it is in the form of a conditioner in which the carrier comprises from 0.1% by weight to 20.0% by weight of a lipid vehicle material, preferably selected from cetyl alcohol, stearyl alcohol, cetyl palmitate, glyceryl monostearate, and mixtures thereof; and from 0.05% by weight to 5.0% by weight of a cationic surfactant, preferably a quaternary ammonium surfactant.
9. A hair care composition according to any of Claims 1-6 characterized in that it is in a form selected from hair sprays, mousses, hair tonics and gels.
10. A method of conditioning and styling hair characterized in that it comprises applying to the hair an effective amount of the composition according to any of Claims 1-9.

# Patentansprüche

1. Haarpflegezusammensetzung, dadurch gekennzeichnet, daß sie
- (a) 0,1 Gew.-% bis 10,0 Gew.-% eines Silikon enthaltenden Copolymers mit einem Molekulargewicht von 10.000 bis 1.000.000, welches eine Komponente umfaßt, die unter: einem lipophilen frei-radikalisch polymerisierbaren Vinylmonomer geringer Polarität (A), einem hydrophilen polaren Monomer, welches mit A copolymerisierbar ist, (B), und Gemischen hiervon ausgewählt ist; gemeinsam mit einem Silikon enthaltenden Makromer (C), welches ein Gewichtsmittel-Molekulargewicht von 1.000 bis 50.000 besitzt, welches auf einem Polydimethylsiloxan beruht, das unter

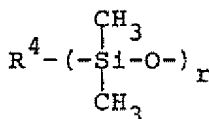


ausgewählt ist, worin m 1, 2 oder 3 bedeutet; p 0 oder 1 ist; R'' für Alkyl oder Wasserstoff steht; q eine ganze Zahl von 2 bis 6 ist; s eine ganze Zahl von 0 bis 2 darstellt; X für



steht;

R<sup>1</sup> Wasserstoff oder -COOH bedeutet; R<sup>2</sup> Wasserstoff, Methyl oder -CH<sub>2</sub>COOH ist; Z für



steht;



R<sup>4</sup> Alkyl, Alkoxy, Alkylamino, Aryl oder Hydroxyl bedeutet; und r eine ganze Zahl von 5 bis 700 ist; und worin das Silikon enthaltende Copolymer 0 Gew.-% bis 98 Gew.-% an Monomer A, 0 Gew.-% bis 98 Gew.-% an Monomer B und 0,1 Gew.-% bis 50 Gew.-% an Monomer C enthält; und

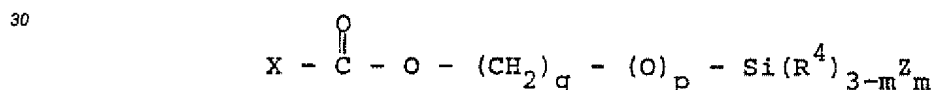
(b) 0,5 Gew.-% bis 99,5 Gew.-% eines Trägers umfaßt, welcher zur Aufbringung auf Haar geeignet ist.

2. Haarpflegezusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das Silikon enthaltende Copolymer 5 Gew.-% bis 98 Gew.-% an Monomer A, 7,5 Gew.-% bis 80 Gew.-% an Monomer B und 0,1 Gew.-% bis 50 Gew.-% an Monomer C umfaßt.

3. Haarpflegezusammensetzung nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Monomer A unter Acrylsäureestern von C<sub>1</sub>-C<sub>18</sub>-Alkoholen, Methacrylsäureestern von C<sub>1</sub>-C<sub>18</sub>-Alkoholen, Styrol, Polystyrolmakromer, Vinylacetat, Vinylchlorid, Vinylpropionat, Vinylidenchlorid, alpha-Methylstyrol, tert. Butylstyrol, Butadien, Cyclohexadien, Ethylen, Propylen, Vinyltoluol, und Gemischen hievon ausgewählt ist; und vorzugsweise unter n-Butylmethacrylat, Isobutylmethacrylat, 2-Ethylhexylmethacrylat, Methylmethacrylat, tert. Butylacrylat, tert. Butylmethacrylat, und Gemischen hievon ausgewählt ist.

4. Haarpflegezusammensetzung nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß das Monomer B unter Acrylsäure, Methacrylsäure, N,N-Dimethylacrylamid, Dimethylaminoethylmethacrylat, quaternisiertem Dimethylaminoethylmethacrylat, Methacrylamid, N-tert. Butylacrylamid, Maleinsäure, Maleinsäureanhydrid, Halbestern von Maleinsäureanhydrid, Crotonsäure, Itaconsäure, Acrylamid, Acrylalkoholen, Hydroxyethylmethacrylat, Diallyldimethylammoniumchlorid, Vinylpyrrolidon, Vinylethern, Maleinimiden, Vinylpyridin, Vinylimidazol, Styrolsulfonat, Allylalkohol, Vinylalkohol, Vinylcaprolactam, und Gemischen hievon ausgewählt ist; und vorzugsweise unter Acrylsäure, N,N-Dimethylacrylamid, Dimethylaminoethylmethacrylat, quaternisiertem Dimethylaminoethylmethacrylat, Vinylpyrrolidon, und Gemischen hievon ausgewählt ist.

5. Haarpflegezusammensetzung nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß das Monomer C die Formel



besitzt, worin p für 0 steht und q 3 ist, m 1 bedeutet, r 250 beträgt, R<sup>4</sup> für Alkyl steht, R<sup>1</sup> Wasserstoff bedeutet und R<sup>2</sup> Methyl darstellt.

6. Haarpflegezusammensetzung nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß das Silikon enthaltende Copolymer unter:  
 Acrylsäure/n-Butylmethacrylat/Polydimethylsiloxan (PDMS)-Makromer - MG 20.000 (10/70/20);  
 N,N-Dimethylacrylamid/Isobutylmethacrylat/PDMS-Makromer - MG 20.000 (20/60/20);  
 Dimethylaminoethylmethacrylat/Isobutylmethacrylat/2-Ethylhexylmethacrylat/PDMS-Makromer - MG 20.000 (25/40/15/20);  
 Dimethylaminoethylmethacrylat/Isobutylmethacrylat/PDMS-Makromer - MG 20.000 (10/70/20);  
 quaternisiertem Dimethylaminoethylmethacrylat/Isobutylmethacrylat/PDMS-Makromer - MG 20.000 (40/40/20);  
 Acrylsäure/Methylmethacrylat/PDMS-Makromer - MG 20.000 (40/40/20);  
 Acrylsäure/Isopropylmethacrylat/PDMS-Makromer - MG 20.000 (25/65/10);  
 N,N-Dimethylacrylamid/Methoxyethylmethacrylat/PDMS-Makromer - MG 20.000 (60/25/15);  
 Dimethylacrylamid/PDMS-Makromer - MG 20.000 (80/20)  
 und Gemischen hievon ausgewählt ist.

7. Haarpflegezusammensetzung nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß sie in der Form eines Shampoos vorliegt, welches zusätzlich 10 Gew.-% bis 30 Gew.-% eines synthetischen grenzflächenaktiven Mittels enthält, welches vorzugsweise unter Alkylsulfaten, ethoxylierten Alkylsulfaten und Gemischen hievon ausgewählt ist.

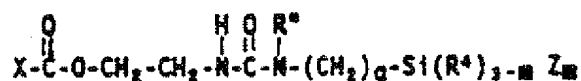
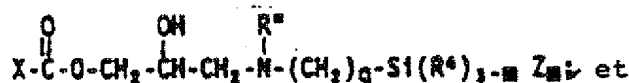
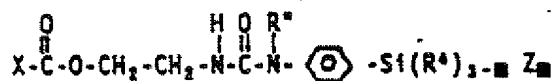
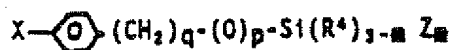
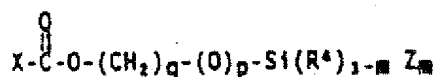
8. Haarpflegezusammensetzung nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß sie in der Form eines Konditionierungsmittels vorliegt, worin der Träger 0,1 Gew.-% bis 20,0 Gew.-% eines Lipidträgermaterials, welches vorzugsweise unter Cetylalkohol, Stearylalkohol, Cetylpalmitat,

Glycerylmonostearat und Gemischen hiervon ausgewählt ist; und 0,05 Gew.-% bis 5,0 Gew.-% eines kationischen grenzflächenaktiven Mittels, vorzugsweise ein quaternäres Ammonium-grenzflächenaktives Mittel, enthält.

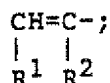
9. Haarpflegezusammensetzung nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß sie in einer Form vorliegt, die unter Haarsprays, -schäumen, Haartonika und -gelen ausgewählt ist.
10. Verfahren zum Haarkonditionieren und -formen, dadurch gekennzeichnet, daß es das Aufbringen einer wirksamen Menge der Zusammensetzung nach einem der Ansprüche 1 bis 9 auf Haar umfaßt.

## Revendications

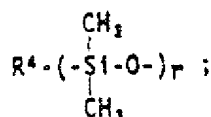
1. Composition de soin de cheveux, caractérisée en ce qu'elle comprend:  
(a) de 0,1% en poids à 10,0% en poids d'un copolymère contenant une silicone, ayant un poids moléculaire de 10.000 à 1.000.000, comprenant un composant choisi parmi: un monomère vinylique lipophile de faible polarité, polymérisable par polymérisation radicalaire (A), un monomère polaire hydrophile copolymérisable avec A (B), et leurs mélanges, ainsi qu'un macromère contenant une silicone (C) ayant un poids moléculaire moyen en poids de 1.000 à 50.000 d'un polydiméthylsiloxane choisi parmi



où m est égal à 1, 2 ou 3; p est égal à 0 ou 1; R" est un groupe alkyle ou un atome d'hydrogène; q est un nombre entier de 2 à 6; s est un nombre entier de 0 à 2; X est



R<sup>1</sup> est un atome d'hydrogène ou un groupe -COOH; R<sup>2</sup> est un atome d'hydrogène, un groupe méthyle ou -CH<sub>2</sub>COOH; Z est



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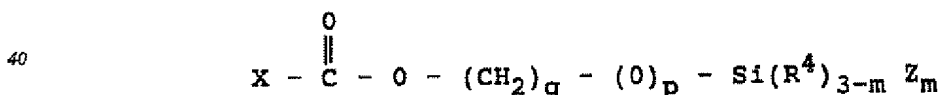
10  $R^4$  est un groupe alkyle, alcoxy, alkylamino, aryle ou hydroxyle; et  $r$  est un nombre entier de 5 à 700; et où le copolymère contenant une silicone comprend de 0% à 98% en poids de monomère A, de 0% à 98% en poids de monomère B et de 0,1% en poids à 50% en poids de monomère C; et (b) de 0,5% en poids à 99,5% en poids d'un véhicule convenant à l'application sur les cheveux.

15 2. Composition de soin des cheveux selon la revendication 1, caractérisée en ce que le copolymère contenant une silicone comprend de 5% en poids à 98% en poids de monomère A, de 7,5% en poids à 80% en poids de monomère B et de 0,1% en poids à 50% en poids de monomère C.

20 3. Composition de soin des cheveux selon la revendication 1 ou 2, caractérisée en ce que le monomère A est choisi parmi les esters d'acide acrylique et d'alcools en  $C_1-C_{16}$ , les esters d'acide méthacrylique et d'alcools en  $C_1-C_{16}$ , le styrène, un macromère polystyrène, l'acétate de vinyle, le chlorure de vinyle, le propionate de vinyle, le chlorure de vinylidène, l' $\alpha$ -méthylstyrène, le t-butylstyrène, le butadiène, le cyclohexadiène, l'éthylène, le propylène, le vinyltoluène, et leurs mélanges; et est de préférence choisi parmi le méthacrylate de n-butyle, le méthacrylate d'isobutyle, le méthacrylate de 2-éthylhexyle, le méthacrylate de méthyle, l'acrylate de t-butyle, le méthacrylate de t-butyle, et leurs mélanges.

25 4. Composition de soin des cheveux selon l'une quelconque des revendications 1-3, caractérisée en ce que le monomère B est choisi parmi l'acide acrylique, l'acide méthacrylique, le N,N-diméthylacrylamide, le méthacrylate de diméthylaminoéthyle, le méthacrylate de diméthylaminoéthyle quaternisé, le méthacrylamide, le N-t-butylacrylamide, l'acide maléique, les demi-esters d'anhydride maléique, l'acide crotonique, l'acide itaconique, l'acrylamide, les alcools d'acrylate, le méthacrylate d'hydroxyéthyle, le chlorure de diallyldiméthylammonium, la vinylpyrrolidone, les éthers vinyliques, les maléimides, la vinylpyridine, le vinylimidazole, les styrène-sulfonate, l'alcool allylique, l'alcool vinylique, le vinylicaprolactame, et leurs mélanges; et est de préférence choisi parmi l'acide acrylique, le N,N-diméthylacrylamide, le méthacrylate de diméthylaminoéthyle, le méthacrylate de diméthylaminoéthyle quaternisé, la vinylpyrrolidone, et leurs mélanges.

35 5. Composition de soin des cheveux selon l'une quelconque des revendications 1-4, caractérisée en ce que le monomère C a pour formule:



45 dans laquelle  $p = 0$  et  $q = 3$ ,  $m$  est égal à 1,  $r$  est égal à 250,  $R^4$  est un groupe alkyle,  $R^1$  est un atome d'hydrogène et  $R^2$  est un groupe méthyle.

6. Composition de soin de cheveux selon l'une quelconque des revendications 1-5, caractérisée en ce que le copolymère contenant une silicone est choisi parmi les séquences suivantes:

50 acide acrylique/méthacrylate de n-butyle/macromère polydiméthylsiloxane (PDMS) - P.M. 20.000 (510/70/20)

N,N-diméthylacrylamide/méthacrylate d'isobutyle/macromère PDMS - P.M. 20.000 (20/60/20);

méthacrylate de diméthylaminoéthyle/méthacrylate d'isobutyle/méthacrylate de 2-éthylhexyle/macromère PDMS - P.M. 20.000 (25/40/15/20);

méthacrylate de diméthylaminoéthyle/méthacrylate d'isobutyle/macromère PDMS - P.M. 20.000 (10/70/20);

55 méthacrylate de diméthylaminoéthyle quaternisé/méthacrylate d'isobutyle/macromère PDMS - P.M. 20.000 (40/40/20);

acide acrylique/méthacrylate de méthyle/macromère PDMS - P.M. 20.000 (40/40/20);

acide acrylique/méthacrylate d'isopropyle/macromère PDMS P.M. 20.000 (25/65/10);

N,N-diméthylacrylamide/méthacrylate de méthoxyéthyle/macromère PDMS - P.M. 20.000 (60/25/15); diméthylacrylamide/macromère PDMS - P.M. 20.000 (80/20); et leurs mélanges.

- 5 7. Composition de soin des cheveux selon l'une quelconque des revendications 1-6, caractérisée en ce qu'elle se trouve sous la forme d'un shampooing qui comprend, en outre, de 10% en poids à 30% en poids d'un tensioactif synthétique, qui est de préférence choisi parmi les alkylsulfates, les alkylsulfates éthoxylés, et leurs mélanges.
- 10 8. Composition de soin des cheveux selon l'une quelconque des revendications 1-6, caractérisée en ce qu'elle se trouve sous la forme d'un conditionneur dans lequel le véhicule comprend de 0,1% en poids à 20,0% en poids d'un véhicule, choisi de préférence parmi l'alcool cétylique, l'alcool stéarylique, le palmitate de cétyle, le monostéarate de glycéryle, et leurs mélanges; et de 0,05% en poids à 5,0% en poids d'un tensioactif cationique, de préférence d'un tensioactif d'ammonium quaternaire.
- 15 9. Composition de soin des cheveux selon l'une quelconque des revendications 1-6, caractérisée en ce qu'elle se trouve sous une forme choisie parmi les laques, mousses, toniques et gels pour les cheveux.
- 20 10. Procédé de conditionnement et de coiffage des cheveux, caractérisé en ce qu'il comprend l'application sur les cheveux d'une quantité efficace de la composition selon l'une quelconque des revendications 1-9.

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**EP 0 412 704 B1**

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A61K 7/08, A61K 7/11

(21) Application number: 90308388.9

(22) Date of filing: 31.07.1990

**(54) Hair conditioning and styling compositions**

Haarpflege- und Fixierungsmittel

Compositions pour traiter et fixer la chevelure

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US-A- 4 693 935	US-A- 4 834 972

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**EP 0 412 704 B1**

## Description

[0001] The present invention relates to hair care compositions which have improved hair conditioning and style retention properties while still leaving the hair with a natural non-sticky feel. These compositions utilize a group of specific silicone macromer-containing copolymers.

[0002] The desire to have hair retain a particular shape is widely held. Such style retention is generally accomplished by either of two routes: permanent chemical alteration or temporary alteration of hair style/shape. A temporary alteration is one which can be removed by water or by shampooing. Temporary style alteration has generally been accomplished by means of the application of a composition to dampened hair after shampooing and/or conditioning and prior to drying and/or styling. The materials used to provide setting benefits have generally been resins or gums and have been applied in the form of mousses, gels, lotions, or sprays. This approach presents several significant drawbacks to the user. It requires a separate step following shampooing/conditioning to apply the styling composition. In addition, since the style hold is provided by resin materials which set-up on the hair, the hair tends to feel sticky or stiff after application and it is difficult to restyle the hair without further application of the styling composition.

[0003] It has now been discovered that hair care compositions comprising certain specifically-defined silicone macromer-containing copolymers provide excellent hair style retention benefits, together with hair conditioning. The compositions may be in any of the conventional forms including, but not limited to, shampoos, conditioners, hair sprays, tonics, lotions, gels, and mousses. The compositions provide these benefits to hair without leaving the hair with a stiff or sticky/tacky feel and without negatively affecting dry hair properties, such as ease of combing. Further, hair to which the compositions of the present invention have been applied may be restyled several times without requiring reapplication of the compositions.

[0004] The results are surprising since other materials which have been typically used in hair care compositions to provide style retention, such as resins and gums, generally hurt dry hair properties (e.g., combing) and leave hair with a sticky and/or stiff feel. Furthermore, silicone materials typically used for hair conditioning tend to hurt style retention.

[0005] Siloxanes (see, for example, US-A-3,208,911, Oppliger, issued September 28, 1965) and siloxane-containing polymers have been taught for use in hair conditioning compositions. US-A-4,601,902, Fridd et al., issued July 22, 1986, describes hair conditioning or shampoo/conditioner compositions which include a polydiorganosiloxane having quaternary ammonium substituted groups attached to the silicon, and a polydiorganosiloxane having silicon-bonded substituents which are amino-substituted hydrocarbon groups. US-A-4,654,161, Kollmeier et al., issued March 31, 1987, describes a group of organopolysiloxanes containing betaine substituents. When used in hair care compositions, these compounds are said to provide good conditioning, compatibility with anionic components, hair substantivity, and low skin irritation. US-A-4,563,347, Starch, issued January 7, 1986, relates to hair conditioning compositions which include siloxane components containing substituents to provide attachment to hair. JP-A-56-129,300, Lion Corporation, published October 9, 1981, relates to shampoo conditioner compositions which include an organopolysiloxaneoxy-alkylene copolymer together with an acrylic resin. US-A-4,479,893, Hirota et al., issued October 30, 1984, describes shampoo conditioner compositions containing a phosphate ester surfactant and a silicon derivative (e.g., polyether- or alcohol-modified siloxanes). Polyether-modified polysiloxanes are also disclosed for use in shampoos in US-A-3,957,970, Korkis, issued May 18, 1976. US-A-4,185,087, Morlino, issued January 22, 1980, describes quaternary nitrogen derivatives of trialkylamino hydroxy organosilicon compounds which are said to have superior hair conditioning properties.

[0006] Siloxane-derived materials have also been used in hair styling compositions. JP-A-56-092,811, Lion Corporation, published December 27, 1979, describes hair setting compositions which comprise an amphoteric acrylic resin, a polyoxyalkylene-denatured organopolysiloxane, and polyethylene glycol. US-A-4,744,978, Homan et al., issued May 17, 1988, describes hair styling compositions (such as hair sprays) which include the combination of a carboxyfunctional polydimethylsiloxane and a cationic organic polymer containing amine or ammonium groups. Hair styling compositions which include polydiorganosiloxanes and a cationic organic polymer are taught in US-A-4,733,677, Gee et al., issued March 29, 1988, and US-A-4,724,851, Cornwall et al., issued February 16, 1988. Finally, EP-A-117,360, Cantrell et al., published September 5, 1984, discloses compositions, containing a siloxane polymer having at least one nitrogen-hydrogen bond, a surfactant, and a solubilized titanate, zirconate or germanate, which act as both a conditioner and a hair styling aid.

[0007] Siloxane-containing polymers have also been used in non-hair care applications. US-A-4,136,250, Mueller et al., issued January 23, 1979, relates to polymeric materials used in biological contexts where oxygen permeable and tissue compatible membranes are required. They can also be used as carriers for biologically-active substances. These materials are hydrophilic water-insoluble gels which include a low molecular weight terminal olefinic siloxane macromer and a polymer containing water-soluble monolefinic monomer. US-A-4,693,935, Mazurek, issued September 15, 1987, describes pressure sensitive adhesive compositions which include a copolymer with a vinyl polymeric backbone having grafted thereto polysiloxane moieties. US-A-4,728,571, Clemens et al., issued March 1, 1988, relates to adhesive release coating compositions which comprise polysiloxane-grafted copolymers and blends of those copolymers

with other polymeric materials. None of these last three patents suggest the use of the disclosed siloxane-containing polymers in hair care compositions.

[0008] It is an object of the present invention to formulate hair care compositions which provide effective hair conditioning and style retention properties.

5 [0009] It is also an object of the present invention to formulate hair care compositions which provide conditioning and style retention from a single composition.

[0010] It is a further object of the present invention to formulate hair care compositions which provide good style retention without leaving hair with a stiff or sticky/tacky feel.

[0011] It is a further object of the present invention to provide an improved method for styling and conditioning hair.

10 [0012] These and other objects will become readily apparent from the detailed description which follows.

[0013] Unless otherwise indicated, all percentages and ratios herein are by weight.

[0014] The present invention relates to hair care compositions comprising

15 (a) from 0.1% to 10.0% by weight of a copolymer, having a molecular weight of from 10,000 to 1,000,000, which has a vinyl polymeric backbone having grafted to it monovalent siloxane polymeric moieties, said copolymer being derived by polymerization of C monomers and components selected from the group consisting of A monomers, B monomers, and mixtures thereof wherein:

20 A is at least one free radically polymerizable vinyl monomer, the amount by weight of A monomer, when used, being up to 98% of the total weight of monomers used in making said copolymer;

B is at least one reinforcing monomer copolymerizable with A, the amount by weight of B monomer, when used, being up to 98% of the total weight of monomers used in making said copolymer, said B monomer being selected from polar monomers and macromers, preferably having a Tg or a Tm above -20°C; and

C is a polymeric monomer having a molecular weight of from 1,000 to 50,000 and the general formula

25 
$$X(Y)_nSi(R)_{3-m}(Z)_m$$
 wherein

X is a vinyl group copolymerizable with the A and B monomers

Y is a divalent linking group

30 R is a hydrogen, lower alkyl, aryl or alkoxy

Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least 500, is essentially unreactive under copolymerization conditions, and is pendant from said vinyl polymeric backbone after copolymerization

n is 0 or 1

35 m is an integer from 1 to 3

wherein C comprises from 0.01% to 50% of the total weight of monomers used in making said copolymer;

40 (b) from 0.5% to 99.5% by weight of a carrier suitable for application to hair.

[0015] The essential, as well as the optional, components of the present invention are described below.

#### Silicone-Containing Copolymer

45 [0016] The compositions of the present invention contain from 0.1% to 10.0% by weight, preferably from 0.5% to 8.0% by weight, of specifically-defined silicone-containing copolymers. It is these polymers which provide the unique hair conditioning and hair setting characteristics of the present invention. The polymers should have a weight average molecular weight of from 10,000 to 1,000,000 (preferably from 30,000 to 300,000) and, preferably, have a Tg of at least -20°C. As used herein, the abbreviation "Tg" refers to the glass transition temperature of the non-silicone backbone, and the abbreviation "Tm" refers to the crystalline melting point of the non-silicone backbone, if such a transition exists for a given polymer.

50 [0017] In its broadest sense, the polymers useful in the hair care compositions of the present invention include all properly defined copolymers of silicone with a non-silicone adhesive polymer. To be useful such copolymers should satisfy the following four criteria:

- 55
- (1) when dried the copolymer phase-separates into a discontinuous phase which includes the silicone portion and a continuous phase which includes the non-silicone portion;
  - (2) the silicone portion is covalently attached to the non-silicone portion;

(3) the molecular weight of the silicone portion is from 1,000 to 50,000; and

(4) the non-silicone portion must render the entire copolymer soluble or dispersible in the hair care composition vehicle and permit the copolymer to deposit on hair.

[0018] The most preferred polymers comprise a vinyl polymeric backbone, preferably having a T<sub>g</sub> or a T<sub>m</sub> above -20°C and, grafted to the backbone, a polydimethylsiloxane macromer having a weight average molecular weight of from 1,000 to 50,000, preferably from 5,000 to 40,000, most preferably about 20,000. The polymer is such that when it is formulated into the finished hair care composition, when dried, the polymer phase separates into a discontinuous phase which includes the polydimethylsiloxane macromer and a continuous phase which includes the backbone. It is believed that this phase separation property provides a specific orientation of the polymer on hair which results in the desired hair conditioning and setting benefits. The phase-separating nature of the compositions of the present invention may be determined as follows:

[0019] The polymer is cast as a solid film out of a good solvent (i.e., a solvent which dissolves both the backbone and the silicone). This film is then sectioned and examined by transmission electron microscopy. Microphase separation is demonstrated by the observation of inclusions in the continuous phase. These inclusions should have the proper size to match the size of the silicone chain (typically a few hundred nm or less) and the proper density to match the amount of silicone present. This behavior is well documented in the literature for polymers with this structure (see, for example, S. D. Smith, Ph.D. Thesis, University of Virginia, 1987, and references cited therein).

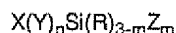
[0020] A second method for determining phase-separating characteristics involves examining the enrichment of the concentration of silicone at the surface of a polymer film relative to the concentration in the bulk polymer. Since the silicone prefers the low energy air interface, it preferentially orients on the polymer surface. This produces a surface which is entirely covered by silicone even when the concentration of the silicone by weight in the whole polymer is low (2% to 20%). This is demonstrated experimentally by ESCA (electron spectroscopy for chemical analysis) of the dried film surface. Such an analysis shows a high level of silicone and a greatly reduced level of backbone polymer when the film surface is analyzed. (Surface here means the first few tens of Angstroms of film thickness.) By varying the angle of the interrogating beam the surface can be analyzed to varying depths.

[0021] Examples of useful copolymers and how they are made are described in detail in US-A-4,693,935, Mazurek, issued September 15, 1987, and US-A-4,728,571, Clemens et al., issued March 1, 1988. These copolymers are comprised of monomers A, C and, optionally, B, which are defined as follows. A is at least one free radically polymerizable vinyl monomer or monomers. B, when used, comprises at least one reinforcing monomer copolymerizable with A and is selected from the group consisting of polar monomers and macromers having a T<sub>g</sub> or a T<sub>m</sub> above -20°C. When used, B may be up to 98%, preferably up to 80%, more preferably up to 20%, of the total monomers in the copolymer. Monomer C comprises from 0.01% to 50.0% of the total monomers in the copolymer.

[0022] Representative examples of A (hydrophobic) monomers are acrylic or methacrylic acid esters of C<sub>1</sub>-C<sub>18</sub> alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 3-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, 1-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, and the like, the alcohols having from about 1-18 carbon atoms with the average number of carbon atoms being from about 4-12; styrene; polystyrene macromer; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene; and mixtures thereof. Preferred A monomers include n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, and mixtures thereof.

[0023] Representative examples of B monomers (hydrophilic) include acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers (such as methyl vinyl ether), maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol (produced by the hydrolysis of vinyl acetate after polymerization) vinyl caprolactam, and mixtures thereof. Preferred B monomers include acrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, and mixtures thereof.

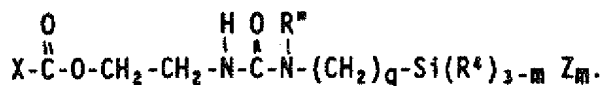
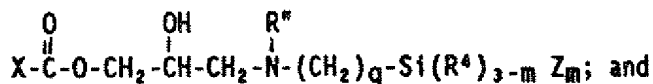
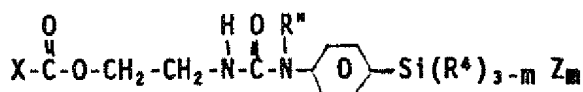
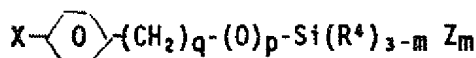
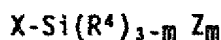
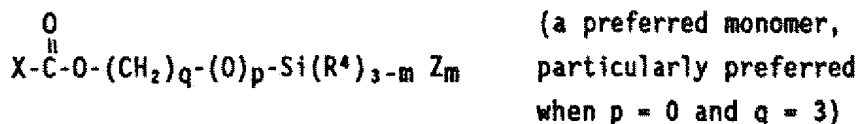
[0024] The C monomer has the general formula



wherein X is a vinyl group copolymerizable with the A and B monomers; Y is a divalent linking group; R is a hydrogen, lower alkyl, aryl or alkoxy; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of



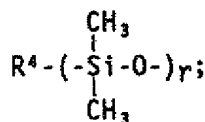
at least 500, is essentially unreactive under copolymerization conditions and is pendant from the vinyl polymeric backbone, described above; n is 0 or 1; and m is an integer from 1 to 3. C has a weight average molecular weight of from 1,000 to 50,000, preferably from 5,000 to 40,000, most preferably from 10,000 to 20,000. Preferably, the C monomer has a formula selected from the following group:



[0025] In those structures, m is 1, 2 or 3 (preferably m = 1); p is 0 or 1; R'' is alkyl or hydrogen; q is an integer from 2 to 6; s is an integer from 0 to 2; X is



R<sup>1</sup> is hydrogen or -COOH (preferably R<sup>1</sup> is hydrogen); R<sup>2</sup> is hydrogen, methyl or -CH<sub>2</sub>COOH (preferably R<sup>2</sup> is methyl); Z is



R<sup>4</sup> is alkyl, alkoxy, alkylamino, aryl, or hydroxyl (preferably R<sup>4</sup> is alkyl); and r is an integer from about 5 to about 700 (preferably r is about 250).

[0026] The polymers of the present invention generally comprise all percentages being expressed by weight of the total weight of monomers used in making the copolymer from 0% to 98% (preferably from 5% to 98%, more preferably from 50% to 90%) of monomer A, from 0% to 98% (preferably from 7.5% to 80%) of monomer B, and from 0.1% to 50% (preferably from 0.5% to 40%, most preferably from 2% to 25%) of monomer C. The combination of the A and B monomers preferably comprises from 50.0% to 99.9% (more preferably 60% to 99%, most preferably from 75% to 95%) of

the polymer. The composition of any particular copolymer will help determine its formulational properties. In fact, by appropriate selection and combination of particular A, B and C components, the copolymer can be optimized for inclusion in specific vehicles. For example, polymers which are soluble in an aqueous formulation preferably have the composition: from 0% to 70% (preferably from 5% to 70%) monomer A, from 30% to 98% (preferably from 30% to 80%) monomer B, and from 1% to 40% monomer C. Polymers which are dispersible have the preferred composition: from 0% to 70% (more preferably from 5% to 70%) monomer A, from 20% to 80% (more preferably from 20% to 60%) monomer B, and from 1% to 40% monomer C.

[0027] In one aspect of the present invention, the polymers comprise from 5% to 98% A monomer, from 0.01% to 50% C monomer, and from 0% to 98% B monomer. In these polymers, it is preferred that A be selected from t-butyl acrylate, t-butyl methacrylate, and mixtures thereof, since such polymers can be dissolved directly in cyclomethicone solvents without requiring co-solvents. This is surprising in view of US-A-4,693,935 (Mazurek) and US-A-4,728,571 (Clemens et al), which suggest that tertiary alcohols are not suitable A monomers.

[0028] Particularly preferred polymers for use in the present invention include the following (the weight percents below refer to the amount of reactants added in the polymerization reaction, not necessarily the amount in the finished polymer):

acrylic acid/n-butylmethacrylate/(polydimethylsiloxane (PDMS) macromer-20,000 molecular weight)  
(10/70/20 w/w/w) (I)

N,N-dimethylacrylamide/isobutyl methacrylate/(PDMS macromer - 20,000 molecular weight)  
(20/60/20 w/w/w) (II)

N,N-dimethylacrylamide/isobutyl methacrylate/2-ethylhexyl methacrylate/(PDMS macromer -  
10,000 molecular weight) (10.5/56/3.5/30 w/w/w/w) (III)

N,N-dimethylacrylamide/(PDMS macromer - 20,000 molecular wt) (80/20 w/w) (IV)

t-butylacrylate/t-butyl methacrylate/(PDMS macromer - 10,000 molecular wt) (56/24/20 w/w/w) (V)

t-butylacrylate/(PDMS macromer-10,000 molecular wt) (80/20 w/w) (IV)

t-butylacrylate/N,N-dimethylacrylamide/(PDMS macromer - 10,000 molecular weight) (70/10/20) (VII)

t-butylacrylate/acrylic acid/(PDMS monomer - 10,000 molecular weight) (75/5/20) (VIII)

[0029] The silicone-containing copolymers described above are synthesized as follows.

[0030] The polymers are synthesized by free radical polymerization methods, the general principles of which are well understood. See, for example, Odian, "Principles of Polymerization", 2nd edition, John Wiley & Sons, 1981, pp. 179-318. The desired monomers are all placed in a reactor, along with a sufficient amount of a mutual solvent so that when the reaction is complete the viscosity of the reaction is reasonable. Typical monomer loadings are from 20% to 50%. Undesired terminators, especially oxygen, are removed as needed. This is done by evacuation or by purging with an inert gas, such as argon or nitrogen. The initiator is introduced and the reaction brought to the temperature needed for initiation to occur, assuming thermal initiators are used. Alternatively, redox or radiation initiation can be used as desired. The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved, typically from a few hours to a few days. The solvent is then removed, usually by evaporation or by precipitating the polymer by addition of a nonsolvent. The polymer is further purified, as needed.

[0031] By way of example, Polymers I, II and III, described above, are synthesized in the following manner. There are numerous variations on these procedures which are entirely up to the discretion of the synthetic chemist (e.g., choice of degassing method and gas, choice of initiator type, extent of conversion, reaction loading, etc). The choice of initiator and solvent are often determined by the requirements of the particular monomers used, since different monomers have different solubilities and different reactivities to a specific initiator.

[0032] Polymer I: Place 10 parts acrylic acid, 70 parts n-butylmethacrylate, and 20 parts 20K PDMS macromer in a flask. Add sufficient ethyl acetate to produce a final monomer concentration of 40%. Add initiator, benzoyl peroxide, to a level of 0.5% by weight relative to the amount of monomer. Evacuate the vessel, and refill with nitrogen. Heat to 60°C and maintain this temperature for 48 hours while agitating. Terminate the reaction by cooling to room temperature, and dry off the ethyl acetate by pouring the reaction mixture into a teflon-coated pan and placing in a vacuum oven.

[0033] Polymer II: Place 20 parts N,N-dimethylacrylamide, 60 parts isobutylmethacrylate, and 20 parts silicone macromer in a reaction vessel fitted with a temperature probe, reflux condenser, inlet port, and argon sparge. Add sufficient

toluene to bring the final monomer concentration to 20% by weight. Sparge with argon for 1 to 2 hours. While sparging, heat to 62°C in a water bath. Add initiator, azobisisobutyronitrile, to a level of 0.25% by weight relative to the weight of monomer present. Maintain temperature at 62°C, with a sufficient rate of argon flow to keep the solution mixed. Monitor the reaction visually, ensuring that no phase separation of reactants occurs during polymerization. If any turbidity is observed, add sufficient warm degassed toluene to eliminate the turbidity. Continue to monitor throughout the reaction. Terminate the reaction after 4 to 6 hours and purify as with Polymer I.

**[0034]** Polymer III: Place 10.5 parts N,N-dimethylmethacrylamide, 56 parts isobutyl methacrylate, 3.5 parts 2-ethyl-hexylmethacrylate, and 30 parts 10K PDMS macromer in a reaction vessel fitted with an argon sparge, temperature probe, reflux condenser and inlet port. Add sufficient toluene or isopropanol to bring the final monomer concentration to 20% by weight. Begin stirring and sparge with argon for 1 hour. While sparging, heat to 60°C in a water bath. Add initiator, azobisisobutyronitrile, to a level of 0.25% (if toluene is the solvent) or 0.125% (if isopropanol is the solvent) by weight relative to the weight of monomer present. Continue stirring and a slow argon sparge and maintain the reaction temperature at 60°C. Allow to react for 6 hours. Terminate the reaction and remove the solvent as with Polymer II.

**[0035]** The compositions of the Invention also comprise a carrier, or a mixture of such carriers, which are suitable for application to hair. The carriers are present at from 0.5% to 99.5%, preferably from 5.0% to 99.5%, most preferably from 10.0% to 90.0% by weight, of the composition. As used herein, the phrase "suitable for application to hair" means that the carrier does not damage or negatively affect the aesthetics of hair or cause irritation to skin. Choice of appropriate solvent will also depend on the particular copolymer to be used, and whether the product formulated is meant to be left on hair (e.g., hair spray, mousse, tonic) or rinsed off (e.g., shampoo, conditioner) after use.

**[0036]** The carriers used herein include solvents, as well as other carrier or vehicle components conventionally used in hair care compositions. The solvent selected must be able to dissolve or disperse the particular silicone copolymer being used. The nature and proportion of B monomer in the copolymer largely determines its polarity and solubility characteristics. The silicone copolymers can be designed, by appropriate combination of monomers, for formulation with a wide range of solvents. Suitable solvents for use in the present invention include, but are not limited to, water, lower alcohols (such as ethanol, isopropanol), hydroalcoholic mixtures, hydrocarbons (such as isobutane, hexane, decene, acetone), halogenated hydrocarbons (such as Freon (RTM)), linalool, hydrocarbon esters (such as ethyl acetate, dibutyl phthalate), volatile silicon derivatives, especially siloxanes (such as phenyl pentamethyl disiloxane, methoxypropyl heptamethyl cyclotetrasiloxane, chloropropyl pentamethyl disiloxane, hydroxypropyl pentamethyl disiloxane, octamethyl cyclotetrasiloxane, decamethyl cyclopentasiloxane), and mixtures thereof. Preferred solvents include water, ethanol, volatile silicon derivatives, and mixtures thereof. The solvents used in such mixtures may be miscible or immiscible with each other.

**[0037]** Where the hair care compositions are conditioner compositions, the carrier may include gel vehicle materials. This gel vehicle comprises two essential components: a lipid vehicle material and a cationic surfactant vehicle material. Cationic surfactant materials are described in detail below. Gel-type vehicles are generally described in the following documents: Barry, "The Self Bodying Action of the Mixed Emulsifier Sodium Dodecyl Sulfate/Cetyl Alcohol", 28 J. of Colloid and Interface Science 82-91 (1968); Barry, et al., "The Self-Bodying Action of Alkyltrimethylammonium Bromides/Cetostearyl Alcohol Mixed Emulsifiers; Influence of Quaternary Chain Length", 35 J. of Colloid and Interface Science 689-708 (1971); and Barry, et al., "Rheology of Systems Containing Cetomacrogol 1000 - Cetostearyl Alcohol, I. Self Bodying Action", 38 J. of Colloid and Interface Science 616-625 (1972).

**[0038]** The vehicles may incorporate one or more lipid vehicle materials which are essentially water-insoluble, and contain hydrophobic and hydrophilic moieties. Lipid vehicle materials include naturally or synthetically-derived acids, acid derivatives, alcohols, esters, ethers, ketones, and amides with carbon chains of from about 12 to about 22, preferably from about 16 to about 18, carbon atoms in length. Fatty alcohols and fatty esters are preferred; fatty alcohols are particularly preferred.

**[0039]** Lipid vehicle materials among those useful herein are disclosed in Bailey's Industrial Oil and Fat Products, (3rd edition, D. Swern, ed., 1979). Fatty alcohols included among those useful herein are disclosed in the following documents: US-A-3,155,591, Hilfer, issued November 3, 1964; US-A-4,165,369, Watanabe, et al., issued August 21, 1979; US-A-4,269,824, Villamarin, et al., issued May 26, 1981; GB-A-1,532,585, published November 15, 1978; and Fukushima, et al., "The Effect of Cetostearyl Alcohol in Cosmetic Emulsions", 98 Cosmetics & Toiletries 89-112 (1983). Fatty esters included among those useful herein are disclosed in US-A-3,341,465, Kaufman, et al., issued September 12, 1976. If included in the compositions of the present invention, the lipid vehicle material is present at from 0.1% to 10.0% by weight of the composition; the cationic surfactant vehicle material is present at from 0.05% to 5.0% by weight of the composition.

**[0040]** Preferred esters for use herein include cetyl palmitate and glycerylmonostearate. Cetyl alcohol and stearyl alcohol are preferred alcohols. A particularly preferred lipid vehicle material is comprised of a mixture of cetyl alcohol and stearyl alcohol containing from 55% to 65% (by weight of mixture) of cetyl alcohol.

**[0041]** Preferred vehicles for use in the compositions of the present invention include combinations of hydrophobically-modified hydroxyethyl cellulose materials with thickeners (such as locust bean gum), particular surfactants, qua-

ternary ammonium compounds (such as ditallowdimethyl ammonium chloride), and/or chelating agents (such as EDTA).

[0042] Other carriers, suitable for use with the present invention are, for example, those used in the formulation of tonics, mousses, gels and hair sprays. Tonics, gels and non-aerosol hair sprays utilize a solvent such as water or alcohol while mousses and aerosol hair sprays additionally utilize a propellant such as trichlorofluoromethane, dichlorodifluoromethane, dimethylether, propane, n-butane or isobutane. A tonic or hair spray product having a low viscosity may also require an emulsifying agent to keep the silicone copolymer homogeneously dispersed in solution. Examples of suitable emulsifying agents include nonionic, cationic, anionic surfactants, or mixtures thereof. If such an emulsifying agent is used, it is present at a level of from 0.25% to 7.5% by weight of the composition. The level of propellant can be adjusted as desired but is generally from 3% to 30% by weight of mousse compositions and from 15% to 50% by weight of the aerosol hair spray compositions.

[0043] The hair care compositions of the present invention may be formulated in a wide variety of product types, including mousses, gels, lotions, tonics, sprays, shampoos and conditioners. The additional components required to formulate such products vary with product type and can be routinely chosen by one skilled in the hair care product art. The following is a description of some of these additional components.

[0044] Surfactants are preferred optional ingredients in the compositions of the invention, particularly shampoo and conditioner compositions. When present, the surfactant comprises from 0.05% to 50% by weight of the composition. For a shampoo, the level is preferably from 10% to 30%, most preferably from 12% to 25% by weight, of the composition. For conditioners, the preferred level of surfactant is from 0.2% to 3% by weight. Surfactants useful in compositions of the present invention include anionic, nonionic, cationic, zwitterionic and amphoteric surfactants.

[0045] Synthetic anionic detergents useful herein, particularly for shampoo compositions, include alkyl and alkyl ether sulfates. These materials have the respective formulae  $\text{ROSO}_3\text{M}$  and  $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$ , wherein R is alkyl or alkenyl of from about 10 to about 20 carbon atoms, x is 1 to 10, and M is a water-soluble cation such as ammonium, sodium, potassium and triethanolamine. The alkyl ether sulfates useful in the present invention are condensation products of ethylene oxide and monohydric alcohols having from about 10 to about 20 carbon atoms. Preferably, R has from about 12 to about 18 carbon atoms in both the alkyl and alkyl ether sulfates. The alcohols can be derived from fats, e.g., coconut oil or tallow, or can be synthetic. Lauryl alcohol and straight chain alcohols derived from coconut oil are preferred herein. Such alcohols are reacted with about 1 to about 10, and especially about 3, molar proportions of ethylene oxide and the resulting mixture of molecular species, having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

[0046] Specific examples of alkyl ether sulfates which may be used in the present invention are sodium coconut alkyl triethylene glycol ether sulfate; sodium tallow alkyl triethylene glycol ether sulfate; and sodium tallow alkyl hexaoxyethylene sulfate. Highly preferred alkyl ether sulfates are those comprising a mixture of individual compounds, said mixture having an average alkyl chain length of from about 12 to about 16 carbon atoms and an average degree of ethoxylation of from about 1 to about 4 moles of ethylene oxide. Such a mixture also comprises from about 0 to about 20% by weight  $\text{C}_{12-13}$  compounds; from about 60 to about 100% by weight of  $\text{C}_{14-15-16}$  compounds, from about 0 to about 20% by weight of  $\text{C}_{17-18-19}$  compounds; from about 3 to about 30% by weight of compounds having a degree of ethoxylation of 0; from about 45 to about 90% by weight of compounds having a degree of ethoxylation of from about 1 to about 4; from about 10 to about 25% by weight of compounds having a degree of ethoxylation of from about 4 to about 8; and from about 0.1 to about 15% by weight of compounds having a degree of ethoxylation greater than about 8.

[0047] Another suitable class of anionic surfactants are the water-soluble salts of the organic, sulfuric acid reaction products of the general formula:



wherein  $\text{R}_1$  is chosen from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 12 to about 18, carbon atoms; and M is a cation. Important examples are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, ineso-, and n-paraffins, having about 8 to about 24 carbon atoms, preferably about 12 to about 18 carbon atoms and a sulfonating agent, e.g.,  $\text{SO}_3$ ,  $\text{H}_2\text{SO}_4$ , oleum, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated  $\text{C}_{12-18}$  n-paraffins.

[0048] Additional examples of anionic synthetic surfactants which come within the terms of the present invention are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other anionic synthetic surfactants of this variety are set forth in US-A-2,486,921; US-A-2,486,922; and US-A-2,396,278.

[0049] Still other anionic synthetic surfactants include the class designated as succinamates. This class includes such surface active agents as disodium N-octadecylsulfosuccinamate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfo-

succinamate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl esters of sodium sulfosuccinic acid.

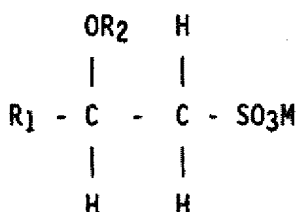
[0050] Other suitable anionic surfactants utilizable herein are olefin sulfonates having about 12 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of  $\alpha$ -olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sultones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid  $\text{SO}_2$ , chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous  $\text{SO}_2$ , etc., when used in the gaseous form.

[0051] The  $\alpha$ -olefins from which the olefin sulfonates are derived are mono-olefins having about 12 to about 24 carbon atoms, preferably about 14 to about 16 carbon atoms. Preferably, they are straight chain olefins. Examples of suitable 1-olefins include 1-dodecene; 1-tetradecene; 1-hexadecene; 1-octadecene; 1-eicosene and 1-tetracosene.

[0052] In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process.

[0053] A specific  $\alpha$ -olefin sulfonate mixture of the above type is described more fully in US-A-3,332,880, Pflaumer and Kessler, issued July 25, 1967.

[0054] Another class of anionic organic surfactants are the  $\beta$ -alkyloxy alkane sulfonates. These compounds have the following formula:



where  $\text{R}_1$  is a straight chain alkyl group having from about 6 to about 20 carbon atoms,  $\text{R}_2$  is a lower alkyl group having from about 1 (preferred) to about 3 carbon atoms, and M is a water-soluble cation as hereinbefore described.

[0055] Specific examples of  $\beta$ -alkyloxy-alkane-1-sulfonates, or alternatively 2-alkyloxy-alkane-1-sulfonates, having low hardness (calcium ion) sensitivity useful herein include: potassium- $\beta$ -methoxydecanesulfonate, sodium 2-methoxytridecanesulfonate, potassium 2-ethoxytetradecylsulfonate, sodium 2-isopropoxyhexadecylsulfonate, lithium 2-t-butoxytetradecyl-sulfonate, sodium  $\beta$ -methoxyoctadecylsulfonate, and ammonium  $\beta$ -n-propoxydodecylsulfonate.

[0056] Many additional nonsoap synthetic anionic surfactants are described in McCutcheon's, Detergents and Emulsifiers, 1984 Annual, published by Allured Publishing Corporation. Also US-A-3,929,678, Laughlin et al., issued December 30, 1975, discloses many other anionic as well as other surfactant types.

[0057] Nonionic surfactants, which are preferably used in combination with an anionic, amphoteric or zwitterionic surfactant, can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. Examples of preferred classes of nonionic surfactants are:

1. The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to from about 10 to about 60 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane, or nonane, for example.

2. Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products which may be varied in composition depending upon the balance between the hydrophobic and hydrophilic elements which is desired. For example, compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of about 2,500 to about 3,000, are satisfactory.

3. The condensation product of aliphatic alcohols having from about 8 to about 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate hav-

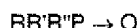
ing from about 10 to about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from about 10 to about 14 carbon atoms.

4. Long chain tertiary amine oxides corresponding to the following general formula:



wherein  $R_1$  contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and  $R_2$  and  $R_3$  contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals. The arrow in the formula is a conventional representation of a semipolar bond. Examples of amine oxides suitable for use in this invention include dimethyl-dodecylamine oxide, oleyldi(2-hydroxyethyl) amine oxide, dimethyloctylamine oxide, dimethyl-decylamine oxide, dimethyl-tetradecylamine oxide, 3,6,9-trioxaheptadecyldiethylamine oxide, di(2-hydroxyethyl)-tetradecylamine oxide, 2-dodecoxyethyl dimethylamine oxide, 3-dodecoxy-2-hydroxypropyldi(3-hydroxypropyl)amine oxide, dimethylhexadecylamine oxide.

5. Long chain tertiary phosphine oxides corresponding to the following general formula:

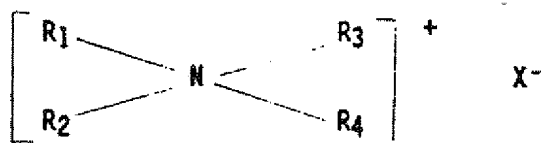


wherein R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety and  $R'$  and  $R''$  are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms. The arrow in the formula is a conventional representation of a semipolar bond. Examples of suitable phosphine oxides are: dodecyldimethylphosphine oxide, tetradecyldimethylphosphine oxide, tetradecylmethylethylphosphine oxide, 3,6,9-trioxaoctadecyldimethylphosphine oxide, cetyldimethylphosphine oxide, 3-dodecoxy-2-hydroxypropyldi(2-hydroxyethyl) phosphine oxide, stearyldimethylphosphine oxide, cetyl ethylpropylphosphine oxide, oleyldiethylphosphine oxide, dodecyldiethylphosphine oxide, tetradecyldiethylphosphine oxide, dodecyldipropylphosphine oxide, dodecyldi(hydroxymethyl)phosphine oxide, dodecyldi(2-hydroxyethyl)phosphine oxide, tetradecylmethyl-2-hydroxypropylphosphine oxide, oleyldimethylphosphine oxide, 2-hydroxydodecyldimethylphosphine oxide.

6. Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from about 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety. Examples include: octadecyl methyl sulfoxide, 2-ketotridecyl methyl sulfoxide, 3,6,9-trioxaoctadecyl 2-hydroxyethyl sulfoxide, dodecyl methyl sulfoxide, oleyl 3-hydroxypropyl sulfoxide, tetradecyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

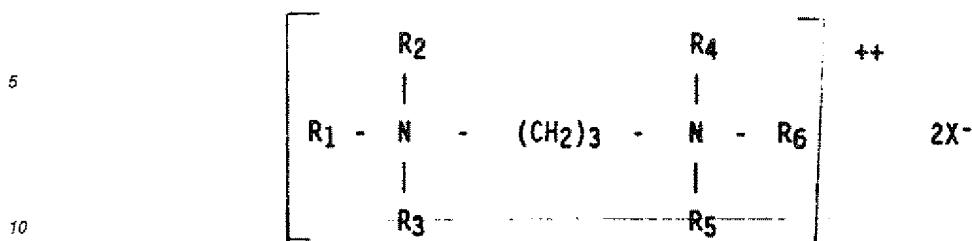
[0058] Cationic surfactants useful in compositions of the present invention, particularly the conditioner compositions, contain amino or quaternary ammonium hydrophilic moieties which are positively charged when dissolved in the aqueous composition of the present invention. Cationic surfactants among those useful herein are disclosed in the following documents: M.C. Publishing Co., McCutcheon's Detergents & Emulsifiers, (North American edition 1979); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; US-A-3,155,591, Hilfer, issued November 3, 1964; US-A-3,929,678, Laughlin, et al., issued December 30, 1975; US-A-3,959,461, Bailey, et al., issued May 25, 1976; and US-A-4,387,090, Bolich, Jr., issued June 7, 1983. If included in the compositions of the present invention, the cationic surfactant is present at from 0.05% to 5% by weight.

[0059] Among the quaternary ammonium-containing cationic surfactant materials useful herein are those of the general formula:



wherein  $R_1$ - $R_4$  are independently an aliphatic group of from about 1 to about 22 carbon atoms, or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having from about 12 to about 22 carbon atoms; and X is an anion selected from halogen, acetate, phosphate, nitrate and alkylsulfate radicals. The aliphatic groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups.

[0060] Other quaternary ammonium salts useful herein have the formula:

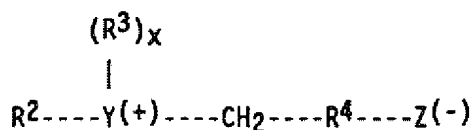


wherein  $R_1$  is an aliphatic group having from about 16 to about 22 carbon atoms,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ , and  $R_6$  are selected from hydrogen and alkyl having from about 1 to about 4 carbon atoms, and X is an ion selected from halogen, acetate, phosphate, nitrate and alkyl sulfate radicals. Such quaternary ammonium salts include tallow propane diammonium dichloride.

[0061] Preferred quaternary ammonium salts include dialkyldimethylammonium chlorides, wherein the alkyl groups have from about 12 to about 22 carbon atoms and are derived from long-chain fatty acids, such as hydrogenated tallow fatty acid (tallow fatty acids yield quaternary compounds wherein  $R_1$  and  $R_2$  have predominately from 16 to 18 carbon atoms). Examples of quaternary ammonium salts useful in the present invention include ditallowdimethyl ammonium chloride, ditallowdimethyl ammonium methyl sulfate, dihexadecyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium chloride, dioctadecyl dimethyl ammonium chloride, dieicosyl dimethyl ammonium chloride, didocosyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium acetate, dihexadecyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium acetate, ditallow dipropyl ammonium phosphate, ditallow dimethyl ammonium nitrate, di(coconutalkyl) dimethyl ammonium chloride, and stearyl dimethyl benzyl ammonium chloride. Ditallow dimethyl ammonium chloride, dicetyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride and cetyl trimethyl ammonium chloride are preferred quaternary ammonium salts useful herein. Di-(hydrogenated tallow) dimethyl ammonium chloride is a particularly preferred quaternary ammonium salt.

[0062] Salts of primary, secondary and tertiary fatty amines are also preferred cationic surfactant materials. The alkyl groups of such amines preferably have from about 12 to about 22 carbon atoms, and may be substituted or unsubstituted. Secondary and tertiary amines are preferred, tertiary amines are particularly preferred. Such amines, useful herein, include stearamido propyl dimethyl amine, diethyl amino ethyl stearamide, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated (5 moles E.O.) stearylamine, dihydroxy ethyl stearylamine, and arachidylbehenylamine. Suitable amine salts include the halogen, acetate, phosphate, nitrate, citrate, lactate and alkyl sulfate salts. Such salts include stearylamine hydrochloride, soyamine chloride, stearylamine formate, N-tallowpropane diamine dichloride and stearamidopropyl dimethylamine citrate. Cationic amine surfactants included among those useful in the present invention are disclosed in US-A-4,275,055, Nachtigal, et al., issued June 23, 1981.

[0063] Zwitterionic surfactants, useful in shampoos as well as conditioners, are exemplified by those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



wherein  $R^2$  contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms;  $R^3$  is an alkyl or monohydroxyalkyl group containing about 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom;  $R^4$  is an alkylene or hydroxyalkylene of from about 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

[0064] Examples of such surfactants include:

4-[N,N-di(2-hydroxyethyl)-N-octadecylammonio]-butane-1-carboxylate;  
 5-[S-3-hydroxypropyl-S-hexadecylsulfonio]-3-hydroxypentane-1-sulfate;  
 3-[P,P-diethyl-P-3,6,9-trioxatetradecoxylphosphonio]-2-hydroxy-propane-1-phosphate;  
 3-[N,N-dipropyl-N-3-dodecoxy-2-hydroxypropylammonio]-propane-1-phosphonate;  
 3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate;  
 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate;  
 4-[N,N-di(2-hydroxyethyl)-N-(2-hydroxydodecyl)ammonio]-butane-1-carboxylate;  
 3-[S-ethyl-S-(3-dodecoxy-2-hydroxypropyl)sulfonio]-propane-1-phosphate;  
 3-[P,P-dimethyl-P-dodecylphosphonio]-propane-1-phosphonate; and  
 5-[N,N-di(3-hydroxypropyl)-N-hexadecylammonio]-2-hydroxy-pentane-1-sulfate.

[0065] Other zwitterionics such as betaines are also useful in the present invention. Examples of betaines useful herein include the high alkyl betaines, such as coco dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alpha-carboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl bis-(2-hydroxyethyl) carboxymethyl betaine, stearyl bis-(2-hydroxypropyl) carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, and lauryl bis-(2-hydroxypropyl)alpha-carboxyethyl betaine. The sulfobetaines may be represented by coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxyethyl) sulfopropyl betaine and the like; amidobetaines and amidosulfobetaines, wherein the  $\text{RCONH}(\text{CH}_2)_3$  radical is attached to the nitrogen atom of the betaine are also useful in this invention.

[0066] Examples of amphoteric surfactants which can be used in the compositions of the present invention are those which are broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecyl-aminopropionate, sodium 3-dodecylaminopropane sulfonate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of US-A-2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of US-A-2,438,091, and the products sold under the trade name "Miranol" (RTM) and described in US-A-2,528,378.

[0067] The above-mentioned surfactants can be used alone or in combination in the hair care compositions of the present invention. The alkyl sulfates, ethoxylated alkyl sulfates, and mixtures thereof are preferred for use herein.

[0068] The hair care compositions herein can contain a variety of other optional components suitable for rendering such compositions more cosmetically or aesthetically acceptable or to provide them with additional usage benefits. Such conventional optional ingredients are well-known to those skilled in the art, e.g., pearlescent aids, such as ethylene glycol distearate; preservatives, such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; thickeners and viscosity modifiers, such as a diethanolamide of a long chain fatty acid (e.g., PEG 3 lauric diethanolamide), cocomonooethanol amide, dimethicone copolyols, guar gum, methyl cellulose, starches and starch derivatives; fatty alcohols, such as cetearyl alcohol; sodium chloride; sodium sulfate; polyvinyl alcohol; ethyl alcohol; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, and sodium carbonate; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents, such as the thioglycolates; perfumes; sequestering agents, such as disodium ethylenediamine tetra-acetate; and polymer plasticizing agents, such as glycerin and propylene glycol. Such optional ingredients generally are used individually at levels of from 0.01% to 10.0%, preferably from 0.05% to 5.0% by weight, of the composition.

[0069] The pH of the present compositions should be between about 3 and about 9, preferably between about 4 and about 8.

[0070] As with all compositions, the present invention should not contain components which unduly interfere with the performance of the compositions.

[0071] The hair care compositions of the present invention can be made using conventional formulation and mixing techniques. Methods of making various types of hair care compositions are described more specifically in the following examples.

[0072] The hair care compositions of the present invention are used in conventional ways to provide the hair conditioning/styling/hold benefits of the present invention. Such method of use depends upon the type of composition employed but generally involves application of an effective amount of the product to the hair, which may then be rinsed from the hair (as in the case of shampoos and some conditioning products) or allowed to remain on the hair (as in the case of spray, mousse, gel, and tonic products). By "effective amount" is meant an amount sufficient to provide the hair conditioning/styling/hold benefits desired considering the length and texture of the hair, and the type of product used. Preferably, the product is applied to wet or damp hair prior to drying and styling of the hair. After the compositions of the present invention are applied to the hair, the hair is dried and styled in the usual ways of the user.



[0073] The following examples further illustrate preferred embodiments within the scope of the present invention.

[0074] The following table defines the silicone copolymers used in the examples (weight ratios given refer to proportion added to reaction mix):

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Copolymer #1	10/70/20 acrylic acid/n-butylmethacrylate/silicone macromer S2, polymer molecular weight about 100,000
Copolymer #2	10/70/20 dimethylacrylamide/isobutyl methacrylate/silicone macromer S2, polymer molecular weight about 400,000
Copolymer #3	60/20/20 diallyldimethyl ammonium chloride/isobutyl methacrylate/silicone macromer S1, polymer molecular weight about 500,000
Copolymer #4	40/40/20 acrylic acid/methyl methacrylate/silicone macromer S1, polymer molecular weight about 400,000
Copolymer #5	10/70/20 acrylic acid/n-butyl methacrylate/silicone macromer S1, polymer molecular weight about 300,000
Copolymer #6	25/65/10 acrylic acid/isopropyl methacrylate/silicone macromer S2, polymer molecular weight about 200,000
Copolymer #7	60/25/15 N,N-dimethylacrylamide/methoxyethyl methacrylate/silicone macromer S1, polymer molecular weight about 200,000
Copolymer #8	12/64/4/20 N,N-dimethylacrylamide/isobutyl methacrylate/2-ethylhexyl methacrylate/PDMS macromer S1, polymer molecular weight about 300,000
Copolymer #9	30/40/10/20 dimethylacrylamide/isobutyl methacrylate/2-ethylhexyl methacrylate/PDMS macromer S1, polymer molecular weight about 300,000
Copolymer #10	80/20 t-butylacrylate/PDMS macromer S2, polymer molecular weight about 150,000

[0075] Silicone macromer S1- has a molecular weight of about 20,000 and is prepared in a manner similar to Example C-2c of US-A-4,728,571, Clemens, issued March 1, 1988.

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[0076] Silicone macromer S2- has a molecular weight of about 10,000 and is prepared in a manner similar to Example C-2b of US-A-4,728,571, Clemens, issued March 1, 1988.

#### EXAMPLE I

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[0077] The following is a hair spray composition representative of the present invention.

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Component	Weight %
Silicone Copolymer #4	2.00
Ethanol	72.90
Perfume	0.10
Isobutane propellant	25.00

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[0078] This product is prepared by adding the silicone copolymer and perfume to the ethanol and mixing for several hours until all the polymer is dissolved. This "concentrate" is then placed in aerosol cans which are fitted with valves crimped under vacuum and then filled through the valve stem with isobutane dispensed by a pressure filler.

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#### EXAMPLE II

[0079] The following is a shampoo composition representative of the present invention.

Component	Weight %
Styling Agent	
Silicone Copolymer #2	1.00
Chloropropyl heptamethyl cyclotetrasiloxane	3.00
Premix	
Silicone gum	0.50
Dimethicone, 350 cs. fluid	0.50
Main Mix	
Ammonium lauryl sulfate	11.00
Cocamide MEA	2.00
Ethylene glycol distearate	1.00
Xanthan gum	1.20
Kathon CG <sup>1</sup> (RTM)	0.04
Citric acid to pH 4.5	q.s.
Double reverse osmosis (DRO) H <sub>2</sub> O	q.s.

<sup>1</sup> preservative commercially available from Rohm & Haas

[0080] The Styling Agent and Premix are blended separately in a conventional manner. The Main Mix is prepared by first dissolving the xanthan gum in the water with conventional mixing. The remaining Main Mix ingredients are added and the Main Mix is heated to 51°C (150°F) with agitation for 1/2 hour. The Styling Agent and Premix are then added sequentially with about ten minutes agitation between additions, and the entire mixture is stirred while the batch is cooled to room temperature. For varied particle size, the Styling Agent and Premix can be added at different times using either or both high shear mixing (high speed dispersator) or normal agitation.

### EXAMPLE III

[0081] The following is a shampoo composition representative of the present invention.

Component	Weight %
Ammonium lauryl sulfate	7.00
Ammonium laureth sulfate	7.00
Cocamide MEA	2.50
Silicone Copolymer #3	1.00
Natrosol 250H <sup>1</sup> (RTM)	1.00
Glydant <sup>2</sup>	0.37
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> hydroxyethyl cellulose commercially available from Aqualon Co.

<sup>2</sup> preservative commercially available from Glyco, Inc.

[0082] The shampoo is made by first dispersing the Natrosol and silicone copolymer in the water for about 1 hour with

conventional agitation. The remaining ingredients are then added.

#### EXAMPLE IV

5 [0083] The following is a styling rinse composition representative of the present invention.

10	Component	Weight %
	Styling Agent Premix	
	Silicone Copolymer #8	2.00
	Phenethylpentamethyl disiloxane	6.00
15	Octamethyl cyclotetrasiloxane	3.00
	Xanthan Premix	
	Xanthan gum	0.25
20	DRO H <sub>2</sub> O	25.00
	Main Mix	
	Dihydrogenated tallow-dimethylammonium chloride (DTDMAC)	0.50
	EDTA, disodium salt	0.10
25	D.C. 929 <sup>1</sup>	2.00
	Perfume	0.10
	Poly Surf C <sup>2</sup> (RTM)	0.75
30	Locust bean gum	0.75
	Kathon CG <sup>3</sup>	0.04
	DRO H <sub>2</sub> O	q.s.

<sup>1</sup> amodimethicone, commercially available from Dow Corning

35 <sup>2</sup> hydrophobically-modified hydroxyethyl cellulose, commercially available from Aqualon Co.

<sup>3</sup> preservative commercially available from Rohm and Haas

40 [0084] The Styling Agent and Xanthan Premixes are blended separately in a conventional manner. The Main Mix is prepared by adding all the ingredients together and heating with agitation to 95°C for about 1/2 hour. As the batch is cooled, the Styling Agent and Xanthan Premixes are added at about 60°C with vigorous mixing. The batch is then cooled to ambient temperature.

#### EXAMPLE V

45 [0085] The following is a styling rinse composition representative of the present invention.

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Component	Weight %
Premix A	
Silicone Copolymer #3	2.00
DRO H <sub>2</sub> O	10.00
Premix B	
Silicone Copolymer #4	2.00
DRO H <sub>2</sub> O	15.00
NaOH solution (50%)	0.20
Main Mix	
Poly Surf C <sup>1</sup> (RTM)	1.00
Stearamide DEA	0.50
Ethanol	10.00
Perfume	0.20
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> hydrophobically-modified hydrox-  
ethyl cellulose, commercially avail-  
able from Aqualon Co.

[0086] Both premixes are blended separately in a conventional manner. The Main Mix is prepared by adding all the ingredients together and heating to about 60°C with mixing. The premixes are then added to the Main Mix with agitation for about 1/2 hour and the batch is cooled to ambient temperature. Either sodium hydroxide or citric acid, if necessary, is added to adjust composition to pH 6.5.

#### EXAMPLE VI

[0087] The following is a hair grooming tonic composition representative of the present invention.

Component	Weight %
Silicone Copolymer #9	0.70
Perfume	0.10
Ethanol	q.s.

[0088] The composition is made by mixing the above components together in a conventional manner.

#### EXAMPLE VII

[0089] The following is a shampoo composition representative of the present invention.

Component	Weight %
Ammonium laureth sulfate	7.00
Cocamido propyl betaine	6.00
Silicone Copolymer #6	2.00
Ethanol	10.00
PEG 150 distearate	2.00
Glydant <sup>1</sup>	0.38
Perfume	1.00
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> preservative commercially available from Glyco, Inc.

[0090] The shampoo is prepared by combining the ammonium laureth sulfate (normally supplied as a 28% solution in water) and Silicone Copolymer and heating to 70°C for about 1/2 hour with mixing. The remaining ingredients are added and mixed for an additional 1/2 hour. The batch is then cooled to ambient temperature. Composition pH is adjusted to 6.3 by the addition of citric acid or sodium hydroxide, if necessary.

#### EXAMPLE VIII

[0091] The following is a styling rinse composition representative of the present invention.

Component	Weight %
Styling Agent	
Silicone Copolymer #5	3.00
Phenylpentamethyl disiloxane	9.00
Premix	
Silicone Gum GE SE76 <sup>1</sup>	0.50
Decamethyl cyclopentasiloxane	4.00
Main Mix	
Poly Surf C <sup>2</sup>	0.60
Locust bean gum	0.50
EDTA, disodium salt	0.15
DTDMAC	0.65
Glydant <sup>3</sup>	0.40
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> Commercially available from General Electric

<sup>2</sup> hydrophobically-modified hydroxyethyl cellulose commercially available from Aqualon Co.

<sup>3</sup> preservative commercially available from Glyco, Inc.

[0092] The Styling Agent and Premix are blended separately by conventional means. The Main Mix is prepared by adding all the ingredients and heating to 95°C for 1/2 hour with agitation. As the batch is cooled to about 60°C, the Premix and Styling Agent mix are added to the Main Mix with agitation and the batch is cooled to ambient temperature.

#### EXAMPLE IX

[0093] The following is a styling rinse composition representative of the present invention.

Component	Weight %
Styling Agent	
Silicone Copolymer #10	3.00
Octamethyl cyclotetrasiloxane	9.00
Premix	
Silicone Gum GE SE 76 <sup>1</sup>	0.50
Decamethyl cyclopentasiloxane	4.00
Main Mix	
Poly Surf C <sup>2</sup> (RTM)	1.25
Stearamide DEA	0.40
DTDMAC	0.50
Kathon CG <sup>3</sup> (RTM)	0.03
Imidazole	0.15
Perfume	0.10
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> Commercially available from General Electric

<sup>2</sup> hydrophobically-modified hydroxyethyl cellulose commercially available from Aqualon Co.

<sup>3</sup> preservative commercially available from Rohm & Haas

[0094] The Styling Agent and Premix are blended separately by conventional means. The Main Mix is prepared by adding all the ingredients and heating to 95°C for 1/2 hour with agitation. As the batch is cooled to about 60°C, the Premix and Styling Agent mixes are added to the Main Mix with agitation and the batch is cooled to ambient temperature.

#### EXAMPLE X

[0095] The following is a cold-wave hair perm composition representative of the present invention.

Component	Weight %
Thioglycolic acid	5.00
Monoethanolamine	6.00
Silicone Copolymer #3	1.50
PEG 10 monostearate	0.50
DRO H <sub>2</sub> O	q.s.

[0096] The composition is prepared by blending all the ingredients with agitation for about 1/2 hour at 60°C and then cooling to ambient temperature.

#### EXAMPLE XI

[0097] The following is a hair conditioner composition representative of the present invention.

Component	Weight %
Styling Agent Premix	
Silicone Copolymer #9	1.00
Phenyl pentamethyl disiloxane	4.00
Silicone Premix	
Silicone gum, GE SE76 <sup>1</sup>	0.30
Octamethyl cyclotetrasiloxane	1.70
Main Mix	
Cetyl alcohol	1.00
Quaternium 18 <sup>2</sup> (RTM)	0.85
Stearyl alcohol (RTM)	0.70
Natrosol 250 MBR <sup>3</sup>	0.50
Ceteareth-20	0.35
Fragrance	0.20
Dimethicone copolyol	0.20
Citric acid	0.13
Methylchloroisothiazolinone, methylisothiazolinone	0.04
Sodium chloride	0.01
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> Commercially available from General Electric

<sup>2</sup> Ditallow quaternary ammonium compound, commercially available from Sherex

<sup>3</sup> hydroxyethyl cellulose material, commercially available from Aqualon Co.

[0098] The product is prepared by combining all the Main Mix ingredients, heating to about 60°C with mixing, and colloid milling down to about 45°C. At this temperature, the two premixes are added separately with moderate agitation and the batch allowed to cool to ambient temperature.

#### EXAMPLE XII

[0099] The following is a styling gel composition representative of the present invention.

Component	Weight %
Silicone Copolymer #7	2.00
Carbopol 940 <sup>1</sup> (RTM)	0.75
Triethanolamine	1.00
Dye solution	0.05
Perfume	0.10
Laureth-23	0.10
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> cross-linked polyacrylic acid, commercially available from B. F. Goodrich

[0100] This batch is made by mixing the listed components together in a conventional manner.

#### EXAMPLE XIII

[0101] The following is a hair mousse composition representative of the present invention.

Component	Weight %
Silicone Copolymer #7	3.00
Ethanol	15.00
Cocamine oxide	0.60
D.C. 190 <sup>1</sup> (RTM)	0.20
Cocamide DEA	0.30
Perfume	0.10
Isobutane	7.00
DRO H <sub>2</sub> O	q.s.

<sup>1</sup> dimethicone copolyol, commercially available from Dow Corning

[0102] The composition is made by blending all of the ingredients except isobutane at ambient temperature until well mixed. Aluminum aerosol cans are then filled with 95 parts of this batch, affixed with a valve which is crimped into position, and lastly pressure filled with 5 parts isobutane.

#### EXAMPLE XIV

[0103] The following is a pump hair spray composition representative of the present invention.

Component	weight %
Silicone Copolymer #1	2.50



(continued)

Component	weight %
Dibutyl phthalate	0.20
Phenyldimethicone	0.30
Perfume	0.05
Aminomethyl propanol	0.20
Ethanol	q.s.

[0104] This composition is made by mixing the listed components together in a conventional manner.

[0105] When the compositions defined in Examples I-IV are applied to hair in the conventional manner, they provide effective hair conditioning and styling/hold benefits without leaving the hair with a sticky/stiff feel.

### Claims

Claims for the following Contracting States : AT, BE, CH, DK, ES, GR, LI, LU, NL, SE

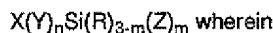
1. A hair care composition characterized in that it comprises (all percentages being on a weight basis):

(a) from 0.1% to 10.0% of a copolymer, having a molecular weight of from 10,000 to 1,000,000, which has a vinyl polymeric backbone having grafted to it monovalent siloxane polymeric moieties, said copolymer being derived by polymerisation of C monomers (which provide the monovalent siloxane polymeric moieties) and components selected from A monomers, B monomers, and mixtures thereof, wherein:

A is at least one free radically polymerisable vinyl monomer, preferably selected from t-butyl acrylate, t-butyl methacrylate, and mixtures thereof, the amount by weight of A monomer, when used, being up to about 98% of the total weight of monomers used in making said copolymer;

B is at least one reinforcing monomer copolymerisable with A, the amount by weight of B monomer, when used being up to about 98% of the total weight of monomers used in making said co-polymer, said B monomer being selected from polar monomers and macromers; and

C is a polymeric monomer having a molecular weight of from 1,000 to 50,000 and the general formula



X is a vinyl group copolymerizable with the A and B monomers

Y is a divalent linking group

R is a hydrogen, lower alkyl, aryl or alkoxy

Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least 500, is essentially unreactive under copolymerisation conditions, and is pendant from said vinyl polymeric backbone after polymerization

n is 0 or 1

m is an integer from 1 to 3

wherein C comprises from 0.01% to 50%, of the total weight of monomers used in making said copolymer; and

(b) from 0.5% to 99.5% of a carrier suitable for application to hair.

2. A hair care composition according to Claim 1 characterized in that the copolymer is derived by polymerisation of from 5% to 98% A monomer, from 0.01% to 50% C monomer and from 0% to 98% B monomer, the percentages being by weight of the total monomer used in making this copolymer.

3. A hair care composition according to Claim 1 characterized in that the copolymer is derived by polymerisation of from 0% to 98% A monomer, from 0.01% to 50% C monomer, and from 7.5% to 80% B monomer, the percentages being by weight of the total monomer used in making the copolymer.

4. A hair care composition according to any of Claims 1 to 3 wherein the polymeric monomer C is a polydimethylsiloxane macromer having a weight average molecular weight between 1,000 and 50,000; and wherein the polymer and carrier are selected such that, when dried, the polymer phase separates into a discontinuous phase which includes the polydimethylsiloxane macromer and a continuous phase which includes the backbone.
5. A hair care composition according to any of Claims 1-4 characterized in that it is in the form of a shampoo which additionally comprises from 10% to 30% of a synthetic surfactant, preferably selected from alkyl sulfates, ethoxylated alkyl sulfates, and mixtures thereof.
6. A hair care composition according to any of Claims 1-4 characterized in that it is in the form of a conditioner in which the carrier comprises from 0.1% to 10.0% of a lipid vehicle material, preferably selected from cetyl alcohol, stearyl alcohol, cetyl palmitate, glyceryl monostearate, and mixtures thereof; and from 0.05% to 5.0% of a cationic surfactant, preferably a quaternary ammonium surfactant.
7. A hair care composition according to any of Claims 1-4 characterized in that it is in a form selected from hair sprays, mousses, hair tonics, and gels.
8. A method of conditioning and styling hair characterized in that it comprises applying to the hair an effective amount of the composition according to any of Claims 1-7.

**Claims for the following Contracting States : DE, FR, GB, IT**

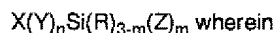
1. A hair care composition characterised in that it comprises (all percentages being on a weight basis):

(a) from 0.1% to 10.0% of a copolymer, having a molecular weight of from 10,000 to 1,000,000, which has a vinyl polymeric backbone having grafted to it monovalent siloxane polymeric moieties, said copolymer being derived by polymerisation of C monomers (which provide the monovalent siloxane polymeric moieties) and components selected from A monomers, B monomers, and mixtures thereof, wherein:

A is at least one free radically polymerisable vinyl monomer, preferably selected from t-butyl acrylate, t-butyl methacrylate, and mixtures thereof, the amount by weight of A monomer, when used, being up to about 98% of the total weight of monomers used in making said copolymer;

B is at least one reinforcing monomer copolymerisable with A, the amount by weight of B monomer, when used, being up to about 98% of the total weight of monomers used in making said copolymer, said B monomer being selected from polar monomers and macromers; and

C is a polymeric monomer having a molecular weight of from 1,000 to 50,000 and the general formula



X is a vinyl group copolymerisable with the A and B monomers

Y is a divalent linking group

R is a hydrogen, lower alkyl, aryl or alkoxy

Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least 500, is essentially unreactive under copolymerisation conditions, and is pendant from said vinyl polymeric backbone after polymerisation

n is 0 or 1

m is an integer from 1 to 3

wherein C comprises from 0.01% to 50%, of the total weight of monomers used in making said copolymer; and

(b) from 0.5% to 99.5% of a carrier suitable for application to hair, but excluding such compositions either wherein monomer B is present or wherein monomer A is t-butyl methacrylate with tridecyl methacrylate.

2. A hair care composition according to claim 1 characterised in that the copolymer is derived by polymerisation of from 5% to 98% A monomer, from 0.01% to 50% C monomer and from 0% to 98% B monomer, the percentages being by weight of the total monomer used in making this copolymer.

3. A hair care composition according to claim 1 characterised in that the copolymer is derived by polymerisation of from 0% to 98% A monomer, from 0.01% to 50% C monomer, and from 7.5% to 80% B monomer, the percentages being by weight of the total monomer used in making the copolymer.
- 5 4. A hair care composition according to any of claims 1 to 3 wherein the polymeric monomer C is a polydimethylsiloxane macromer having a weight average molecular weight between 1,000 and 50,000; and wherein the polymer and carrier are selected such that, when dried, the polymer phase separates into a discontinuous phase which includes the polydimethylsiloxane macromer and a continuous phase which includes the backbone.
- 10 5. A hair care composition according to any of claims 1 to 4 characterised in that it is in the form of a shampoo which additionally comprises from 10% to 30% of a synthetic surfactant, preferably selected from alkyl sulfates, ethoxylated alkyl sulfates, and mixtures thereof.
6. A hair care composition according to any of claims 1 to 5 in which monomer A comprises t-butyl acrylate.
- 15 7. A hair care composition according to any of claims 1 to 6 in which monomer A is t-butyl acrylate alone or mixed with t-butyl methacrylate.
8. A hair care composition according to any of claims 1-7 characterised in that it is in the form of a conditioner in which the carrier comprises from 0.1% to 10.0% of a lipid vehicle material, preferably selected from cetyl alcohol, stearyl alcohol, cetyl palmitate, glyceryl monostearate, and mixtures thereof; and from 0.05% to 5.0% of a cationic surfactant, preferably a quaternary ammonium surfactant.
- 20 9. A hair care composition according to any of claims 1-7 characterised in that it is in a form selected from hair sprays, mousses, hair tonics, and gels.
- 25 10. A method of conditioning and styling hair characterised in that it comprises applying to the hair an effective amount of the composition according to any of claims 1-9.
- 30 11. A hair care composition characterised in that it comprises (all percentages being on a weight basis):
  - (a) from 0.1% to 10.0% of a copolymer, having a molecular weight of from 10,000 to 1,000,000, which has a vinyl polymeric backbone having grafted to it monovalent siloxane polymeric moieties, said copolymer being derived by polymerisation of C monomers (which provide the monovalent siloxane polymeric moieties) and components selected from A monomers, B monomers, and mixtures thereof, wherein:
    - A is at least one free radically polymerisable vinyl monomer, preferably selected from t-butyl acrylate, t-butyl methacrylate, and mixtures thereof, the amount by weight of A monomer, when used, being up to about 98% of the total weight of monomers used in making said copolymer;
    - 40 B is at least one reinforcing monomer copolymerisable with A, the amount by weight of B monomer, when used, being up to about 98% of the total weight of monomers used in making said copolymer, said B monomer being selected from polar monomers and macromers; and
    - C is a polymeric monomer having a molecular weight of from 1,000 to 50,000 and the general formula
 
$$X(Y)_nSi(R)_{3-m}(Z)_m \text{ wherein}$$
      - X is a vinyl group copolymerisable with the A and B monomers
      - Y is a divalent linking group
      - R is a hydrogen, lower alkyl, aryl and alkoxy
      - 50 Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least 500, is essentially unreactive under copolymerisation conditions, and is pendant from said vinyl polymeric backbone after polymerisation
      - n is 0 or 1
      - m is an integer from 1 to 3
- 55 wherein C comprises from 0.01% to 50%, of the total weight of monomers used in making said copolymer; and

(b) from 0.5% to 99.5% of a carrier suitable for application to hair, but excluding such compositions wherein the copolymer is derived by polymerisation of both a C monomer wherein the siloxane polymeric moiety has 150 or fewer siloxane units and a B monomer in an amount by weight of 15% or greater based on the total weight of monomers used in making the copolymer.

12. A hair care composition according to claim 11 characterised in that the copolymer is derived by polymerisation of from 5% to 98% A monomer, from 0.01% to 50% C monomer and from 0% to 98% B monomer, the percentages being by weight of the total monomer used in making this copolymer.
13. A hair care composition according to claim 11 characterised in that the copolymer is derived by polymerisation of from 0% to 98% A monomer, from 0.01% to 50% C monomer, and from 7.5% to 80% B monomer, the percentages being by weight of the total monomer used in making the copolymer.
14. A hair care composition according to any of claims 11 to 13 wherein the polymeric monomer C is a polydimethylsiloxane macromer having a weight average molecular weight between 1,000 and 50,000; and wherein the polymer and carrier are selected such that, when dried, the polymer phase separates into a discontinuous phase which includes the polydimethylsiloxane macromer and a continuous phase which includes the backbone.
15. A hair care composition according to any of claims 11-14 characterised in that it is in the form of a shampoo which additionally comprises from 10% to 30% of a synthetic surfactant, preferably selected from alkyl sulfates, ethoxylated alkyl sulfates, and mixtures thereof.
16. A hair care composition according to any of claims 11-14 characterised in that it is in the form of a conditioner in which the carrier comprises from 0.1% to 10.0% of a lipid vehicle material, preferably selected from cetyl alcohol, stearyl alcohol, cetyl palmitate, glyceryl monostearate, and mixtures thereof; and from 0.05% to 5.0% of a cationic surfactant, preferably a quaternary ammonium surfactant.
17. A hair care composition according to any of claims 11-14 characterised in that it is in a form selected from hair sprays, mousses, hair tonics, and gels.
18. A method of conditioning and styling hair characterised in that it comprises applying to the hair an effective amount of the composition according to any of claims 11-17.

#### Patentansprüche

Patentansprüche für folgende Vertragsstaaten : AT, BE, CH, DK, ES, GR, LI, LU, NL, SE

1. Haarpflegezusammensetzung, dadurch gekennzeichnet, daß sie (wobei sich alle Prozentsätze auf das Gewicht beziehen) :

(a) 0,1% bis 10,0% von einem Copolymer mit einem Molekulargewicht von 10.000 bis zu 1.000.000, welches ein Vinylpolymerrückgrat besitzt, an das einwertige Siloxanpolymerreste gepfropft sind, welches Copolymer durch Polymerisation von C-Monomeren (welche die einwertigen Siloxanpolymerreste bereitstellen) und unter A-Monomeren, B-Monomeren und Gemischen hiervon ausgewählten Komponenten erhalten wird, worin:

A mindestens ein freiradikalisch polymerisierbares Vinylmonomer ist, welches vorzugsweise unter tert. Butylacrylat, tert. Butylethacrylat und Gemischen hiervon ausgewählt ist, wobei die Gewichtsmenge an A-Monomer, wenn es eingesetzt wird, bis zu etwa 98% des Gesamtgewichts der bei der Herstellung des genannten Copolymers verwendeten Monomeren beträgt;

B mindestens ein mit A copolymerisierbares, verstärkendes Monomer ist, wobei die Gewichtsmenge an B-Monomer, wenn es eingesetzt wird, bis zu etwa 98% des Gesamtgewichts der zur Herstellung des genannten Copolymers verwendeten Monomeren beträgt, welches B-Monomer unter polaren Monomeren und Makromeren ausgewählt ist; und

C ein polymeres Monomer mit einem Molekulargewicht von 1.000 bis 50.000 und der allgemeinen Formel  $X(Y)_nSi(R)_{3-m}(Z)_m$  ist, worin

X eine mit den A- und B-Monomeren copolymerisierbare Vinylgruppe darstellt,

Y eine zweiwertige verbindende Gruppe bedeutet,

5 R für Wasserstoff, Niederalkyl, Aryl oder Alkoxy steht,

Z ein einwertiger Siloxanpolymerrest mit einem Zahlenmittel-Molekulargewicht von mindestens 500 ist, welcher unter Copolymerisationsbedingungen im wesentlichen unreaktiv ist und sich nach der Polymerisation vom genannten Vinylpolymerrückgrat weg erstreckt,

10 n 0 oder 1 beträgt,

m eine ganze Zahl von 1 bis 3 ist,

15 worin C 0,01% bis 50% des Gesamtgewichts an zur Herstellung des genannten Copolymers verwendeten Monomeren darstellt; und

(b) 0,5% bis 99,5% von einem Träger umfaßt, welcher für die Aufbringung auf das Haar geeignet ist.

- 20 2. Haarpflegezusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das Copolymer durch Polymerisation von 5% bis 98% A-Monomer, 0,01% bis 50% C-Monomer und 0% bis 98% B-Monomer erhalten wird, wobei sich die Prozentsätze auf das Gewicht des zur Herstellung dieses Copolymers verwendeten gesamten Monomeren beziehen.
- 25 3. Haarpflegezusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das Copolymer durch Polymerisation von 0% bis 98% A-Monomer, 0,01% bis 50% C-Monomer und 7,5% bis 80% B-Monomer erhalten wird, wobei sich die Prozentsätze auf das Gewicht des zur Herstellung des Copolymers verwendeten gesamten Monomeren beziehen.
- 30 4. Haarpflegezusammensetzung nach einem der Ansprüche 1 bis 3, worin das polymere C-Monomer ein Polydimethylsiloxanmakromer mit einem Gewichtsmittel-Molekulargewicht von 1.000 bis 50.000 ist; und worin das Polymer und der Träger derart ausgewählt sind, daß sich die polymere Phase, wenn sie getrocknet ist, in eine das Polydimethylsiloxanmakromer enthaltende, diskontinuierliche Phase und in eine das Rückgrat enthaltende, kontinuierliche Phase aufteilt.
- 35 5. Haarpflegezusammensetzung nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß sie in der Form eines Shampoos vorliegt, welches zusätzlich 10% bis 30% von einem synthetischen grenzflächenaktiven Mittel umfaßt, das vorzugsweise unter Alkylsulfaten, ethoxylierten Alkylsulfaten und Gemischen hiervon ausgewählt ist.
- 40 6. Haarpflegezusammensetzung nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß sie in der Form eines Konditionierungsmittels vorliegt, worin der Träger 0,1% bis 10,0% von einem Lipidträgermaterial, welches vorzugsweise unter Cetylalkohol, Stearylalkohol, Cetylpalmitat, Glycerylmonostearat und Gemischen hiervon ausgewählt ist, und 0,05% bis 5,0% von einem kationischen grenzflächenaktiven Mittel, vorzugsweise einem quaternären grenzflächenaktiven Mittel auf Basis von Ammonium umfaßt.
- 45 7. Haarpflegezusammensetzung nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß sie in einer Form vorliegt, welche unter Haarsprays, Schäumen, einem Haartonikum und Gelen ausgewählt ist.
- 50 8. Verfahren zur Konditionierung und Formgebung von Haar, dadurch gekennzeichnet, daß es das Aufbringen einer wirksamen Menge der Zusammensetzung nach einem der Ansprüche 1 bis 7 auf das Haar umfaßt.

#### Patentansprüche für folgende Vertragsstaaten : DE, FR, GB, IT

- 55 1. Haarpflegezusammensetzung, dadurch gekennzeichnet, daß sie (wobei sich alle Prozentsätze auf das Gewicht beziehen):
  - (a) 0,1% bis 10,0% von einem Copolymer mit einem Molekulargewicht von 10.000 bis zu 1.000.000, welches ein Vinylpolymerrückgrat besitzt, an das einwertige Siloxanpolymerreste gefropft sind, welches Copolymer

durch Polymerisation von C-Monomeren (welche die einwertigen Siloxanpolymerreste bereitstellen) und unter A-Monomeren, B-Monomeren und Gemischen hiervon ausgewählten Komponenten erhalten wird, worin:

A mindestens ein freiradikalisch polymerisierbares Vinylmonomer ist, welches vorzugsweise unter tert. Butylacrylat, tert. Butylmethacrylat und Gemischen hiervon ausgewählt ist, wobei die Gewichtsmenge an A-Monomer, wenn es eingesetzt wird, bis zu etwa 98% des Gesamtgewichts der bei der Herstellung des genannten Copolymers verwendeten Monomeren beträgt;

B mindestens ein mit A copolymerisierbares, verstärkendes Monomer ist, wobei die Gewichtsmenge an B-Monomer, wenn es eingesetzt wird, bis zu etwa 98% des Gesamtgewichts der zur Herstellung des genannten Copolymers verwendeten Monomeren beträgt, welches B-Monomer unter polaren Monomeren und Makromeren ausgewählt ist; und

C ein polymeres Monomer mit einem Molekulargewicht von 1.000 bis 50.000 und der allgemeinen Formel  $X(Y)_nSi(R)_{3-m}(Z)_m$  ist, worin

X eine mit den A- und B-Monomeren copolymerisierbare Vinylgruppe darstellt,

Y eine zweiwertige verbindende Gruppe bedeutet,

R für Wasserstoff, Niederalkyl, Aryl oder Alkoxy steht,

Z ein einwertiger Siloxanpolymerrest mit einem Zahlenmittel-Molekulargewicht von mindestens 500 ist, welcher unter Copolymerisationsbedingungen im wesentlichen unreaktiv ist und sich nach der Polymerisation vom genannten Vinylpolymerrückgrat weg erstreckt,

n 0 oder 1 beträgt,

m eine ganze Zahl von 1 bis 3 ist,

worin C 0,01% bis 50% des Gesamtgewichts an zur Herstellung des genannten Copolymers verwendeten Monomeren darstellt; und

(b) 0,5% bis 99,5% von einem Träger umfaßt, welcher für die Aufbringung auf das Haar geeignet ist, wobei aber solche Zusammensetzungen ausgeschlossen sind, worin das B-Monomer vorhanden ist oder worin das A-Monomer tert. Butylmethacrylat mit Tridecylmethacrylat darstellt.

2. Haarpflegezusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das Copolymer durch Polymerisation von 5% bis 98% A-Monomer, 0,01% bis 50% C-Monomer und 0% bis 98% B-Monomer erhalten wird, wobei sich die Prozentsätze auf das Gewicht des zur Herstellung dieses Copolymers verwendeten gesamten Monomeren beziehen.
3. Haarpflegezusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das Copolymer durch Polymerisation von 0% bis 98% A-Monomer, 0,01% bis 50% C-Monomer und 7,5% bis 80% B-Monomer erhalten wird, wobei sich die Prozentsätze auf das Gewicht des zur Herstellung des Copolymers verwendeten gesamten Monomeren beziehen.
4. Haarpflegezusammensetzung nach einem der Ansprüche 1 bis 3, worin das polymere C-Monomer ein Polydimethylsiloxanmakromer mit einem Gewichtsmittel-Molekulargewicht von 1.000 bis 50.000 ist; und worin das Polymer und der Träger derart ausgewählt sind, daß sich die polymere Phase, wenn sie getrocknet ist, in eine das Polydimethylsiloxanmakromer enthaltende, diskontinuierliche Phase und in eine das Rückgrat enthaltende, kontinuierliche Phase auf trennt.
5. Haarpflegezusammensetzung nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß sie in der Form eines Shampoos vorliegt, welches zusätzlich 10% bis 30% von einem synthetischen grenzflächenaktiven Mittel umfaßt, das vorzugsweise unter Alkylsulfaten, ethoxylierten Alkylsulfaten und Gemischen hiervon ausgewählt ist.
6. Haarpflegezusammensetzung nach einem der Ansprüche 1 bis 5, worin das A-Monomer tert. Butylacrylat umfaßt.

7. Haarpflegezusammensetzung nach einem der Ansprüche 1 bis 6, worin das A-Monomer tert. Butylacrylat allein oder im Gemisch mit tert. Butylmethacrylat ist.

8. Haarpflegezusammensetzung nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß sie in der Form eines Konditionierungsmittels vorliegt, worin der Träger 0,1% bis 10,0% von einem Lipidträgermaterial, welches vorzugsweise unter Cetylalkohol, Stearylalkohol, Cetylpalmitat, Glycerylmonostearat und Gemischen hievon ausgewählt ist, und 0,05% bis 5,0% von einem kationischen grenzflächenaktiven Mittel, vorzugsweise einem quaternären grenzflächenaktiven Mittel auf Basis von Ammonium umfaßt.

9. Haarpflegezusammensetzung nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß sie in einer Form vorliegt, welche unter Haarsprays, Schäumen, einem Haartonikum und Gelen ausgewählt ist.

10. Verfahren zur Konditionierung und Formgebung von Haar, dadurch gekennzeichnet, daß es das Aufbringen einer wirksamen Menge der Zusammensetzung nach einem der Ansprüche 1 bis 9 auf das Haar umfaßt.

11. Haarpflegezusammensetzung, dadurch gekennzeichnet, daß sie (wobei sich alle Prozentsätze auf das Gewicht beziehen):

(a) 0,1% bis 10,0% von einem Copolymer mit einem Molekulargewicht von 10.000 bis zu 1.000.000, welches ein Vinylpolymerrückgrat besitzt, an das einwertige Siloxanpolymerreste gepfropft sind, welches Copolymer durch Polymerisation von C-Monomeren (welche die einwertigen Siloxanpolymerreste bereitstellen) und unter A-Monomeren, B-Monomeren und Gemischen hievon ausgewählten Komponenten erhalten wird, worin:

A mindestens ein freiradikalisch polymerisierbares Vinylmonomer ist, welches vorzugsweise unter tert. Butylacrylat, tert. Butylmethacrylat und Gemischen hievon ausgewählt ist, wobei die Gewichtsmenge an A-Monomer, wenn es eingesetzt wird, bis zu etwa 98% des Gesamtgewichts der bei der Herstellung des genannten Copolymers verwendeten Monomeren beträgt;

B mindestens ein mit A copolymerisierbares, verstärkendes Monomer ist, wobei die Gewichtsmenge an B-Monomer, wenn es eingesetzt wird, bis zu etwa 98% des Gesamtgewichts der zur Herstellung des genannten Copolymers verwendeten Monomeren beträgt, welches B-Monomer unter polaren Monomeren und Makromeren ausgewählt ist; und

C ein polymeres Monomer mit einem Molekulargewicht von 1.000 bis 50.000 und der allgemeinen Formel  $X(Y)_nSi(R)_{3-m}(Z)_m$  ist, worin

X eine mit den A- und B-Monomeren copolymerisierbare Vinylgruppe darstellt,

Y eine zweiwertige verbindende Gruppe bedeutet,

R für Wasserstoff, Niederalkyl, Aryl oder Alkoxy steht,

Z ein einwertiger Siloxanpolymerrest mit einem Zahlenmittel-Molekulargewicht von mindestens 500 ist, welcher unter Copolymerisationsbedingungen im wesentlichen unreaktiv ist und sich nach der Polymerisation vom genannten Vinylpolymerrückgrat weg erstreckt,

n 0 oder 1 beträgt,

m eine ganze Zahl von 1 bis 3 ist,

worin C 0,01% bis 50% des Gesamtgewichts an zur Herstellung des genannten Copolymers verwendeten Monomeren darstellt; und

(b) 0,5% bis 99,5% von einem Träger umfaßt, welcher für die Aufbringung auf das Haar geeignet ist, wobei aber solche Zusammensetzungen ausgeschlossen sind, worin das Copolymer durch Polymerisation sowohl eines C-Monomers, in welchem der Siloxanpolymerrest 150 oder weniger Siloxaneinheiten enthält, als auch eines B-Monomers in einer Gewichtsmenge von 15% oder darüber, bezogen auf das Gesamtgewicht der zur Herstellung des Copolymers verwendeten Monomere, erhalten wird.

12. Haarpflegezusammensetzung nach Anspruch 11, dadurch gekennzeichnet, daß das Copolymer durch Polymerisation von 5% bis 98% A-Monomer, 0,01% bis 50% C-Monomer und 0% bis 98% B-Monomer erhalten wird, wobei sich die Prozentsätze auf das Gewicht des zur Herstellung dieses Copolymers verwendeten gesamten Monomeren beziehen.
13. Haarpflegezusammensetzung nach Anspruch 11, dadurch gekennzeichnet, daß das Copolymer durch Polymerisation von 0% bis 98% A-Monomer, 0,01% bis 50% C-Monomer und 7,5% bis 80% B-Monomer erhalten wird, wobei sich die Prozentsätze auf das Gewicht des zur Herstellung des Copolymers verwendeten gesamten Monomeren beziehen.
14. Haarpflegezusammensetzung nach einem der Ansprüche 11 bis 13, worin das polymere C-Monomer ein Polydimethylsiloxanmakromer mit einem Gewichtsmittel-Molekulargewicht von 1.000 bis 50.000 ist; und worin das Polymer und der Träger derart ausgewählt sind, daß sich die polymere Phase, wenn sie getrocknet ist, in eine das Polydimethylsiloxanmakromer enthaltende, diskontinuierliche Phase und in eine das Rückgrat enthaltende, kontinuierliche Phase aufteilt.
15. Haarpflegezusammensetzung nach einem der Ansprüche 11 bis 14, dadurch gekennzeichnet, daß sie in der Form eines Shampoos vorliegt, welches zusätzlich 10% bis 30% von einem synthetischen grenzflächenaktiven Mittel umfaßt, das vorzugsweise unter Alkylsulfaten, ethoxylierten Alkylsulfaten und Gemischen hiervon ausgewählt ist.
16. Haarpflegezusammensetzung nach einem der Ansprüche 11 bis 14, dadurch gekennzeichnet, daß sie in der Form eines Konditionierungsmittels vorliegt, worin der Träger 0,1% bis 10,0% von einem Lipidträgermaterial, welches vorzugsweise unter Cetylalkohol, Stearylalkohol, Cetylpalmitat, Glycerylmonostearat und Gemischen hiervon ausgewählt ist, und 0,05% bis 5,0% von einem kationischen grenzflächenaktiven Mittel, vorzugsweise einem quaternären grenzflächenaktiven Mittel auf Basis von Ammonium umfaßt.
17. Haarpflegezusammensetzung nach einem der Ansprüche 11 bis 14, dadurch gekennzeichnet, daß sie in einer Form vorliegt, welche unter Haarsprays, Schäumen, einem Haartonikum und Gelen ausgewählt ist.
18. Verfahren zur Konditionierung und Formgebung von Haar, dadurch gekennzeichnet, daß es das Aufbringen einer wirksamen Menge der Zusammensetzung nach einem der Ansprüche 11 bis 17 auf das Haar umfaßt.

## Revendications

Revendications pour les Etats contractants suivants : AT, BE, CH, DK, ES, GR, LI, LU, NL, SE

1. Composition de soin des cheveux, caractérisée en ce qu'elle comprend (tous les pourcentages étant pondéraux):

(a) de 0,1% à 10,0% d'un copolymère ayant une masse moléculaire de 10 000 à 1 000 000, qui possède un squelette polymère vinylique sur lequel sont greffés des groupements polymères siloxane monovalents, ledit copolymère étant obtenu par polymérisation de monomères C (qui fournissent les groupements polymères siloxane monovalents) et de constituants choisis parmi les monomères A, les monomères B, et leurs mélanges, dans lequel:

A est au moins un monomère vinylique polymérisable par polymérisation radicalaire, choisi de préférence parmi l'acrylate de t-butyle, le méthacrylate de t-butyle et leurs mélanges, la quantité, en poids, du monomère A, lorsqu'il est utilisé, allant jusqu'à environ 98% du poids total des monomères utilisés pour fabriquer ledit copolymère;

B est au moins un monomère de renfort copolymérisable avec A, la quantité en poids du monomère B, lorsqu'il est utilisé, allant jusqu'à environ 98% du poids total des monomères utilisés pour fabriquer ledit copolymère, ledit monomère B étant choisi parmi les monomères et les macromères polaires; et

C est un monomère polymère ayant une masse moléculaire de 1 000 à 50 000 et répondant à la formule générale  $X(Y)_nSi(R)_{3-m}(Z)_m$ , dans laquelle

X est un groupe vinylique copolymérisable avec les monomères A et B,

Y est un groupe de liaison divalent,

R est un atome d'hydrogène ou un groupe alkyle inférieur, aryle ou alcoxy,

Z est un groupement polymère siloxane monovalent ayant une masse moléculaire moyenne en nom-



bre d'au moins 500, est essentiellement non réactif dans les conditions de copolymérisation et est pendant dudit squelette polymère vinylique après la polymérisation,  
n vaut 0 ou 1,  
m est un nombre entier de 1 à 3,

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dans laquelle C constitue de 0,01% à 50% du poids total des monomères utilisés pour fabriquer ledit copolymère; et

(b) de 0,5% à 99,5% d'un véhicule approprié à l'application sur les cheveux.

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2. Composition de soin des cheveux selon la revendication 1, caractérisée en ce que le copolymère est obtenu par polymérisation de 5% à 98% de monomère A, de 0,01% à 50% de monomère C et de 0% à 98% de monomère B, les pourcentages étant rapportés au poids du total des monomères utilisés pour fabriquer ce copolymère.

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3. Composition de soin des cheveux selon la revendication 1, caractérisée en ce que le copolymère est obtenu par polymérisation de 0% à 98% de monomère A, de 0,01% à 50% de monomère C et de 7,5% à 80% de monomère B, les pourcentages étant rapportés au poids du total des monomères utilisés pour fabriquer ce copolymère.

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4. Composition de soin des cheveux selon l'une quelconque des revendications 1 à 3, dans laquelle le monomère polymère C est un macromère de polydiméthylsiloxane ayant une masse moléculaire moyenne en poids comprise entre 1 000 et 50 000; et dans laquelle le polymère et le véhicule sont choisis de telle sorte qu'une fois séchée, la phase de polymère se sépare en une phase discontinue contenant le macromère de polydiméthylsiloxane et une phase continue contenant le squelette.

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5. Composition de soin des cheveux selon l'une quelconque des revendications 1 à 4, caractérisée en ce qu'elle se présente sous la forme d'un shampoing qui comprend en plus de 10% à 30% d'un tensioactif synthétique, choisi de préférence parmi les alkylsulfates, les alkylsulfates éthoxylés et leurs mélanges.

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6. Composition de soin des cheveux selon l'une quelconque des revendications 1 à 4, caractérisée en ce qu'elle se présente sous la forme d'un produit de conditionnement dans lequel le véhicule comprend de 0,1% à 10,0% d'un matériau véhicule lipidique, choisi de préférence parmi l'alcool cétylique, l'alcool stéarylique, le palmitate de cétyle, le monostéarate de glycéryle, et leurs mélanges; et de 0,05% à 5,0% d'un tensioactif cationique, de préférence un tensioactif de type ammonium quaternaire.

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7. Composition de soin des cheveux selon l'une quelconque des revendications 1 à 4, caractérisée en ce qu'elle se présente sous la forme de pulvérisations pour les cheveux, de mousses, de toniques capillaires ou de gels.

8. Procédé pour conditionner et coiffer les cheveux, caractérisé en ce qu'il comprend l'application sur les cheveux d'une quantité efficace de la composition selon l'une quelconque des revendications 1 à 7.

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**Revendications pour les Etats contractants suivants : DE, FR, GB, IT**

1. Composition de soin des cheveux, caractérisée en ce qu'elle comprend (tous les pourcentages étant pondéraux):

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(a) de 0,1% à 10,0% d'un copolymère ayant une masse moléculaire de 10 000 à 1 000 000, qui possède un squelette polymère vinylique sur lequel sont greffés des groupements polymères siloxane monovalents, ledit copolymère étant obtenu par polymérisation de monomères C (qui fournissent les groupements polymères siloxane monovalents) et de constituants choisis parmi les monomères A, les monomères B, et leurs mélanges, dans lequel:

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A est au moins un monomère vinylique polymérisable par polymérisation radicalaire, choisi de préférence parmi l'acrylate de t-butyle, le méthacrylate de t-butyle et leurs mélanges, la quantité, en poids, du monomère A, lorsqu'il est utilisé, allant jusqu'à environ 98% du poids total des monomères utilisés pour fabriquer ledit copolymère;

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B est au moins un monomère de renfort copolymérisable avec A, la quantité en poids du monomère B, lorsqu'il est utilisé, allant jusqu'à environ 98% du poids total des monomères utilisés pour fabriquer ledit copolymère, ledit monomère B étant choisi parmi les monomères et les macromères polaires; et

C est un monomère polymère ayant une masse moléculaire de 1 000 à 50 000 et répondant à la formule

générale  $X(Y)_nSi(R)_{3-m}(Z)_m$ , dans laquelle

X est un groupe vinylique copolymérisable avec les monomères A et B,

Y est un groupe de liaison divalent,

R est un atome d'hydrogène ou un groupe alkyle inférieur, aryle ou alcoxy,

Z est un groupement polymère siloxane monovalent ayant une masse moléculaire moyenne en nombre d'au moins 500, est essentiellement non réactif dans les conditions de copolymérisation et est pendant dudit squelette polymère vinylique après la polymérisation,

n vaut 0 ou 1,

m est un nombre entier de 1 à 3,

dans laquelle C constitue de 0,01% à 50% du poids total des monomères utilisés pour fabriquer ledit copolymère; et

(b) de 0,5% à 99,5% d'un véhicule approprié à l'application sur les cheveux,

mais à l'exclusion des compositions dans lesquelles le monomère B est présent ou dans lesquelles le monomère A est du méthacrylate de t-butyle avec du méthacrylate de tridécylo.

2. Composition de soin des cheveux selon la revendication 1, caractérisée en ce que le copolymère est obtenu par polymérisation de 5% à 98% de monomère A, de 0,01% à 50% de monomère C et de 0% à 98% de monomère B, les pourcentages étant rapportés au poids du total des monomères utilisés pour fabriquer ce copolymère.

3. Composition de soin des cheveux selon la revendication 1, caractérisée en ce que le copolymère est obtenu par polymérisation de 0% à 98% de monomère A, de 0,01% à 50% de monomère C et de 7,5% à 80% de monomère B, les pourcentages étant rapportés au poids du total des monomères utilisés pour fabriquer ce copolymère.

4. Composition de soin des cheveux selon l'une quelconque des revendications 1 à 3, dans laquelle le monomère polymère C est un macromère de polydiméthylsiloxane ayant une masse moléculaire moyenne en poids comprise entre 1 000 et 50 000; et dans laquelle le polymère et le véhicule sont choisis de telle sorte qu'une fois séchée, la phase de polymère se sépare en une phase discontinue contenant le macromère de polydiméthylsiloxane et une phase continue contenant le squelette.

5. Composition de soin des cheveux selon l'une quelconque des revendications 1 à 4, caractérisée en ce qu'elle se présente sous la forme d'un shampoing qui comprend en plus de 10% à 30% d'un tensioactif synthétique, choisi de préférence parmi les alkylsulfates, les alkylsulfates éthoxylés et leurs mélanges.

6. Composition de soin des cheveux selon l'une quelconque des revendications 1 à 5, dans laquelle le monomère A comprend de l'acrylate de t-butyle.

7. Composition de soin des cheveux selon l'une quelconque des revendications 1 à 6, dans laquelle le monomère A est de l'acrylate de t-butyle, seul ou en mélange avec du méthacrylate de t-butyle.

8. Composition de soin des cheveux selon l'une quelconque des revendications 1 à 7, caractérisée en ce qu'elle se présente sous la forme d'un produit de conditionnement dans lequel le véhicule comprend de 0,1% à 10,0% d'un matériau véhicule lipidique, choisi de préférence parmi l'alcool cétylique, l'alcool stéarylique, le palmitate de cétyle, le monostéarate de glycéryle, et leurs mélanges; et de 0,05% à 5,0% d'un tensioactif cationique, de préférence un tensioactif de type ammonium quaternaire.

9. Composition de soin des cheveux selon l'une quelconque des revendications 1 à 7, caractérisée en ce qu'elle se présente sous la forme de pulvérisations pour les cheveux, de mousses, de toniques capillaires ou de gels.

10. Procédé pour conditionner et coiffer les cheveux, caractérisé en ce qu'il comprend l'application sur les cheveux d'une quantité efficace de la composition selon l'une quelconque des revendications 1 à 9.

11. Composition de soin des cheveux, caractérisée en ce qu'elle comprend (tous les pourcentages étant pondéraux):

(a) de 0,1% à 10,0% d'un copolymère ayant une masse moléculaire de 10 000 à 1 000 000, qui possède un squelette polymère vinylique sur lequel sont greffés des groupements polymères siloxane monovalents, ledit

copolymère étant obtenu par polymérisation de monomères C (qui fournissent les groupements polymères siloxane monovalents) et de constituants choisis parmi les monomères A, les monomères B, et leurs mélanges, dans lequel:

- 5 A est au moins un monomère vinylique polymérisable par polymérisation radicalaire, choisi de préférence parmi l'acrylate de t-butyle, le méthacrylate de t-butyle et leurs mélanges, la quantité, en poids, du monomère A, lorsqu'il est utilisé, allant jusqu'à environ 98% du poids total des monomères utilisés pour fabriquer ledit copolymère;
- 10 B est au moins un monomère de renfort copolymérisable avec A, la quantité en poids du monomère B, lorsqu'il est utilisé, allant jusqu'à environ 98% du poids total des monomères utilisés pour fabriquer ledit copolymère, ledit monomère B étant choisi parmi les monomères et les macromères polaires; et
- C est un monomère polymère ayant une masse moléculaire de 1 000 à 50 000 et répondant à la formule générale  $X(Y)_nSi(R)_{3-m}(Z)_m$ , dans laquelle

- 15 X est un groupe vinyle copolymérisable avec les monomères A et B,  
Y est un groupe de liaison divalent,  
R est un atome d'hydrogène ou un groupe alkyle inférieur, aryle ou alcoxy,  
Z est un groupement polymère siloxane monovalent ayant une masse moléculaire moyenne en nombre d'au moins 500, est essentiellement non réactif dans les conditions de copolymérisation et est
- 20 pendant dudit squelette polymère vinylique après la polymérisation,  
n vaut 0 ou 1,  
m est un nombre entier de 1 à 3,

- 25 dans laquelle C constitue de 0,01% à 50% du poids total des monomères utilisés pour fabriquer ledit copolymère; et

- (b) de 0,5% à 99,5% d'un véhicule approprié à l'application sur les cheveux, mais à l'exclusion des compositions dans lesquelles le copolymère est obtenu par polymérisation à la fois d'un monomère C dans lequel le groupement polymère siloxane possède 150 motifs siloxane ou moins et d'un
- 30 monomère B en proportion pondérale de 15% ou plus, rapportée au poids total des monomères utilisés pour fabriquer le copolymère.

12. Composition de soin des cheveux selon la revendication 11, caractérisée en ce que le copolymère est obtenu par polymérisation de 5% à 98% de monomère A, de 0,01% à 50% de monomère C et de 0% à 98% de monomère B,
- 35 les pourcentages étant rapportés au poids du total des monomères utilisés pour fabriquer ce copolymère.

13. Composition de soin des cheveux selon la revendication 11, caractérisée en ce que le copolymère est obtenu par polymérisation de 0% à 98% de monomère A, de 0,01% à 50% de monomère C et de 7,5% à 80% de monomère B, les pourcentages étant rapportés au poids du total des monomères utilisés pour fabriquer ce copolymère.
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14. Composition de soin des cheveux selon l'une quelconque des revendications 11 à 13, dans laquelle le monomère polymère C est un macromère de polydiméthylsiloxane ayant une masse moléculaire moyenne en poids comprise entre 1 000 et 50 000; et dans laquelle le polymère et le véhicule sont choisis de telle sorte qu'une fois séchée, la phase de polymère se sépare en une phase discontinue contenant le macromère de polydiméthylsiloxane et une
- 45 phase continue contenant le squelette.

15. Composition de soin des cheveux selon l'une quelconque des revendications 11 à 14, caractérisée en ce qu'elle se présente sous la forme d'un shampooing qui comprend en plus de 10% à 30% d'un tensioactif synthétique, choisi de préférence parmi les alkylsulfates, les alkylsulfates éthoxylés et leurs mélanges.
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16. Composition de soin des cheveux selon l'une quelconque des revendications 11 à 14, caractérisée en ce qu'elle se présente sous la forme d'un produit de conditionnement dans lequel le véhicule comprend de 0,1% à 10,0% d'un matériau véhicule lipidique, choisi de préférence parmi l'alcool cétylique, l'alcool stéarylique, le palmitate de cétyle, le monostéarate de glycéryle, et leurs mélanges; et de 0,05% à 5,0% d'un tensioactif cationique, de préférence un tensioactif de type ammonium quaternaire.
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17. Composition de soin des cheveux selon l'une quelconque des revendications 11 à 14, caractérisée en ce qu'elle se présente sous la forme de pulvérisations pour les cheveux, de mousses, de toniques capillaires ou de gels.

18. Procédé pour conditionner et coiffer les cheveux, caractérisé en ce qu'il comprend l'application sur les cheveux d'une quantité efficace de la composition selon l'une quelconque des revendications 11 à 17.

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(54) Title: HAIR TREATMENT COMPOSITIONS WHICH PROVIDE HAIR BODY AND WHICH COMPRISE SILICONE PRESSURE SENSITIVE ADHESIVES

(57) Abstract: An aqueous hair treatment composition comprising: a) at least one silicone pressure sensitive adhesive; and b) at least one material selected from the group consisting of a hair conditioning agent, a hair cleansing agent, and an agent for hair care suspension, is described.



WO 03/028677 A1

HAIR TREATMENT COMPOSITIONS WHICH PROVIDE HAIR BODY AND  
WHICH COMPRISE SILICONE PRESSURE SENSITIVE ADHESIVES

FIELD OF THE INVENTION

5

This invention relates to rinse-off hair treatment compositions and to their use in the treatment of hair.

BACKGROUND AND PRIOR ART

10

Shampoo compositions are generally formulated with highly effective cleansing surfactants, typically anionic surfactants, and do not in themselves provide much conditioning or styling benefit to the hair. In fact, basic shampoo formulations which have not been supplemented with specific conditioning or styling agents have a tendency to leave the hair in a cosmetically-unsatisfactory condition with regards to manageability and stylability. The hair tends to have a harsh, dull and dry feel, often referred to as "creak", is often difficult to comb, in either the wet or the dry state, typically has poor brushing properties, and tends to have poor set-retaining abilities.

This has resulted in the use of products containing specific conditioning and/or styling agents. Such agents are generally applied separately after shampooing and rinsing the hair, for example, in the form of conditioner formulations or styling mousses etc. Alternatively, conditioning and/or styling agents have been incorporated into the shampoo formulations. Although the latter approach provides the advantage of removing the need for a separate

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conditioner or styling treatment, the conditioning and/or styling agents are not always compatible with the shampoo ingredients, especially the anionic surfactant. This can result in the cleansing action and/or cosmetic benefit being  
5 compromised.

One of the most common methods for imparting styling benefits to the hair has been the use of hair fixative agents, such as high molecular weight polymers. The problem  
10 with using such agents is that they have a tendency to negatively impact on conditioning attributes such as wet and dry stage clean feel and smoothness. In fact, they can result in a sticky feel to the hair.

15 Conventional styling polymers are typically water soluble. This means that when incorporated into a shampoo or conditioner which is rinsed off the hair, there is a tendency for the styling polymer to be washed away to a greater or lesser degree with the shampoo/conditioner.  
20 Hence, most styling products are leave-in products which are applied to the hair as post-shampoo/conditioner treatments.

The problem being addressed by the present invention is the provision of rinse-off hair treatment compositions which  
25 impart styling benefits, and in particular body benefits on the hair, but which do not compromise the cleansing action of the shampoo and which do not negatively impact on the conditioning attributes of the hair. The body benefits or attributes the present invention is looking particularly to  
30 provide include root lift, increased hair volume, bounce, control (i.e. ease of styling) and manageability, i.e.

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maintenance of style without undue stiffness and negative sensory feel. Such body attributes are particularly attractive to people with fine or long, weighty hair.

5 One way in which this problem has been addressed in the past has been to include conditioning agents, for example silicones and cationic surfactants, in the compositions, to counter the negative effects of the styling agents. Although such conditioning agents do provide substantial  
10 improvements in for example the wet and dry combing properties of the hair and in the smoothness of the hair, they tend to have a negative effect on many of the attributes associated with hair body.

15 An alternative approach has been the use different forms of styling agents such as small particulate materials. Such an approach is described, for example, in our unpublished PCT International Patent Application No. PCT/GB00/04020. This document describes the use of small hard particles, and in  
20 particular colloidal silica, in hair treatment compositions to impart body and volume to the hair. Although providing significant styling benefits, the use of these materials can still lead to small levels of sensory negatives, such as for example a dry feel to the hair.

25 JP 10144622 (Toshiba Silicone) discloses cosmetic compositions containing particles consisting of colloidal silica cores surrounded by silicone shells which may be used on the skin or hair. Hairdressing lotions, hair creams and  
30 cleansing compositions such as a shampoo, rinse and



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conditioner are disclosed as suitable cosmetic compositions in which the particles can be utilized.

We have now found that the inclusion of a certain level of  
5 silicone pressure sensitive adhesives (silicone PSA) in the hair treatment formulations provides substantial styling benefits, in particular with regards to imparting body attributes to the hair. Furthermore, the conditioning attributes of the hair are not adversely affected by the use  
10 of hair compositions containing these silicone PSA's and there is no necessity to incorporate additional conditioning agents or specialized surfactant systems. The compositions of the present invention are also stable.

15 The incorporation of silicone PSA's into the hair treatment compositions of this invention leads to substantive improvements in the body of the washed and optionally conditioned hair, especially if a subsequent styling regime is followed. The compositions impart body attributes, such  
20 as root lift, volume, bounce and manageability, in the absence (or substantial absence) of a styling polymer, which leads to compositions which have a styling benefit, but nevertheless do not suffer from the sensory negatives (e.g. stickiness and/or dry feel) which are associated with prior  
25 styling compositions which are based on, for example, a styling polymer.

#### SUMMARY OF THE INVENTION

30 Accordingly, this invention provides an aqueous hair treatment composition comprising:

- 5 -

- a) at least one silicone pressure sensitive adhesive
- b) a material selected from the group consisting of a suspending agent, a hair conditioning agent and a hair cleansing agent.

5

Preferably, the resulting hair care composition will increase static friction of dry hair by at least about 10%, and will increase in the dynamic friction of dry hair by no more than 100% or leave said dynamic friction unchanged or  
10 decrease said dynamic friction. This invention provides for the use of silicone PSA's as defined herein in a hair treatment composition to impart body without compromising conditioning.

#### 15 DETAILED DESCRIPTION OF THE INVENTION

Unless specified otherwise, all wt% values quoted hereinafter are percentages by weight based on total weight of the hair treatment composition.

20

Compositions of the invention may be prepared by known methods, or may be prepared by methods which are analogous to known methods.

25 By "insoluble" is meant that the material is not soluble in water (distilled or equivalent) at a concentration of 0.1%, at 25°C.

The invention provides an aqueous hair treatment composition  
30 comprising:

- 6 -

- a) at least one silicone pressure sensitive adhesive
- b) a material selected from the group consisting of a suspending agent, a hair conditioning agent and a hair cleansing agent.

5

Preferably, the resulting hair care composition will increase static friction of dry hair by at least 10%, or more preferably by at least about 15%, most preferably by about 20% and which increases the dynamic friction of dry hair by not more than 100%, or more preferably no more than 60% or most preferably not more than by 40% Said dynamic friction of dry hair may also be unchanged or decrease.

More preferably, the invention provides an aqueous hair treatment composition comprising

- a) about 0.1% to about 10% of at least one silicone pressure sensitive adhesive;  
and
- b1) about 0.1% to about 10% of at least one suspending agent; or
- b2) about 0.05% to about 10% of at least one hair conditioning agent; or
- b3) about 5% to about 40% of at least one hair cleansing agent.

25

What follows now are descriptions of the materials and ingredients that may be employed in the compositions of the present invention.

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## SILICONE PRESSURE SENSITIVE ADHESIVES

Pressure sensitive adhesives (PSA) are being used for a wide variety of adhesive applications. Organic PSAs have been  
5 finding increased utility principally for manufacture of adhesive tapes and labels. Other PSA uses include automotive, medical and coating industry applications. There are several chemical types of PSAs, including tackified natural rubbers, synthetic rubbers, polyvinyl  
10 ether types PSAs, acrylic, and silicone PSAs. The present invention relates to the use of Silicone PSAs in hair care applications.

PSAs require a delicate balance of viscous and elastic  
15 properties that results in desired balance of adhesion, cohesion, peel strength and elasticity. The performance of PSA is governed mainly by three properties: Tack, peel strength and shear strength. Properties such as shear strength, cohesion can be tested using standard tests that  
20 are found in the detail in literature (Ref: A. Zosel, *J. Adhesion*, 1994, 44, pp 1-6). Adhesion is the binding force between two different materials, whereas cohesion is the binding force between two similar materials. When two materials are brought into contact with each other, the  
25 surface molecules interact, giving rise to attractive forces that may be physical, chemical or electrostatic (corresponding to adsorption, covalent bonding or van der Waals forces, respectively). When the molecules are similar, as in the case of two 'glue molecules,' the  
30 cohesive force causes the glue to stick to itself. When the molecules are dissimilar, as in the case of a glue molecule

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and a molecule of the substrate (the surface the glue is sticking to), the adhesive force holds the glue to the substrate. PSAs usually consist of chemical moieties that exhibit varying tackifying and elastomeric behaviors. By  
5 controlling the amount of the viscous and elastic materials, desired properties can be obtained. As used herein, the term PSA shall refer to an adhesive composition that satisfies the Dahlquist criterion, i.e.: 1 -sec creep compliance greater than  $1 \times 10^{-6} \text{ cm}^2/\text{dyne}$  (Ref: Handbook of  
10 Pressure Sensitive Adhesive Technology, p 172, D. Satas (ed.) Van Nostrand, N. Y. (1989)). Typically, a pressure sensitive adhesive is normally tacky at room temperature and adheres to a surface upon contact to the surface without the need for more than finger or hand pressure. Owing to the  
15 unique chemistry of PSAs, they exhibit some unique properties such as low glass transition temperature ( $T_g$ ), low surface energy, high flexibility, quick bonding.

This present invention relates to the use of silicone  
20 PSAs for hair care rinse-off applications. Silicone PSAs comprise two major components, a polymer or gum, and a tackifying resin. The polymer is typically a high molecular weight polydimethylsiloxane or polydimethyldiphenylsiloxane, that contains residual silanol functionality ( $\text{SiOH}$ ) on the  
25 ends of the polymer chain, or a block copolymer comprising polydiorganosiloxane soft segments and urea terminated hard segments. The tackifying resin is generally a three dimensional silicate structure that is endcapped with trimethylsiloxy groups ( $\text{OSiMe}_3$ ) and also contains some  
30 residual silanol functionality. Manufacture of typical

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silicone PSA is described in US patent 2736721 (Dexter).  
Other materials can be added for special purposes, including  
pigments, plasticizers, and fillers. Although, silicone  
PSAs have been cited in US patent 5337047, US patent 5060804  
5 and US patent 5451610.

A preferable silicone PSA can be a mixture of a hydroxy-  
terminated polydimethylsiloxane gum of  $T_g$  below  $-20^\circ\text{C}$  with a  
silicone resin which has a  $T_g$  or softening point above  $0^\circ\text{C}$ .  
10 The gum is lightly crosslinked with the resin. The resin  
comprises at least 30% units selected from  $\text{RSiO}_3/2$  units (T  
units) and  $\text{SiO}_4/2$  units (Q units), optionally together with  
 $\text{R}_3\text{SiO}_1/2$  units (M units) and/or  $\text{R}_2\text{SiO}_2/2$  units (D units),  
where R is a monovalent hydrocarbon radical, preferably  
15 methyl, and generally has an average of at least one R group  
per Si atom. The  $T_g$  of the blend of resin and gum is  
generally between  $-15$  and  $15^\circ\text{C}$  (T at tan delta maximum). The  
resin lowers the rubbery plateau modulus of the system. The  
resin is preferably a silanol-containing trimethylated  
20 silicate resin, that is a resin comprising Q and M units in  
which some trimethylsilyl groups are replaced by  
dimethylhydroxysilyl groups. The PSAs described above can  
be supplied as solutions or in emulsified form to be used in  
the hair care compositions of this invention.

25 A preferred silicone PSA emulsion can be prepared by mixing  
the silicone PSA in volatile silicone fluid. The silicone  
PSA together with a volatile silicone fluid having a boiling  
point below  $300^\circ\text{C}$  is emulsified together in water using one  
30 or more surfactants. The preferred surfactants are anionic

- 10 -

or nonionic surfactants, especially a blend of anionic and nonionic surfactants. The silicone fluid can be a linear polydiorganosiloxane such as hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, dodecamethylpentasiloxane or a polydimethylsiloxane of viscosity 1cSt, or can be a cyclic siloxane such as decamethylcyclopentasiloxane or octamethylcyclotetrasiloxane or can be a mixture of one or more linear polydimethylsiloxanes with one or more cyclic siloxanes.

10

Silicone PSAs may be formed with a wide range of tack properties, peel adhesion properties and cohesion properties. In the hair care compositions of the present invention, it is also preferable that the silicone PSAs have tack and adhesion properties in the following range:

15

	Tack (g)	Adhesion (g/cm)
Low tack (LT)	<70	800
Medium tack (MT)	70	600
High tack (HT)	500	400

In the hair care compositions of the present invention, it is also preferable that the silicone PSAs have tack properties between about 40 g to about 750 g, or more preferably 50 g to 600 g; adhesion properties between about 1600 g/cm to 200 g/cm, or more preferably 1000 g/cm to 300 g/cm.

25

Silicone PSA that may be used in the compositions of the invention may have a resin-to-polymer ratio that can range

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from about 25 to 75 to about 75 to 25, more preferably from about 55 to 45 to 65 to 35.

5 In the hair care compositions of the present invention, the silicone PSAs can cause said compositions to maximally increase the dynamic friction of dry hair by 100% or 60%, or most preferably by 40%; and can cause the static friction of dry hair to increase by at least 10% or 15%, or most preferably by 20%.

10

This invention does not include the silicone acrylate type of PSAs, such as acrylate dimethicone copolymer cited in US patent 5166276 or acrylates/dimethicone methacrylate copolymer that have been previously used in hair care applications.

15

#### HAIR TREATMENT COMPOSITIONS

20 Compositions in accordance with the invention may be formulated as compositions for the treatment of hair and subsequent rinsing.

#### COMPOSITIONS MADE WITH A SUSPENDING AGENT

25 Compositions in accordance with this invention may also be formulated as suspensions for the treatment of hair and subsequent rinsing. These compositions will require silicone PSAs and a suspending agent.



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Suspending agents:

In a preferred embodiment, the hair treatment composition further comprises from 0.01 to 10 wt% of a suspending agent  
5 for the silicone pressure sensitive adhesive. Suitable suspending agents are selected from polyacrylic acids, cross-linked polymers of acrylic acid, copolymers of acrylic acid with a hydrophobic monomer, copolymers of carboxylic acid-containing monomers and acrylic esters, cross-linked  
10 copolymers of acrylic acid and acrylate esters, heteropolysaccharide gums and crystalline long chain acyl derivatives. The long chain acyl derivative is desirably selected from ethylene glycol stearate, alkanolamides of fatty acids having from 16 to 22 carbon atoms and mixtures  
15 thereof. Ethylene glycol distearate and polyethylene glycol 3 distearate are preferred long chain acyl derivatives. Polyacrylic acid is available commercially as Carbopol 420, Carbopol 488 or Carbopol 493. Polymers of acrylic acid cross-linked with a polyfunctional agent may also be used,  
20 they are available commercially as Carbopol 910, Carbopol 934, Carbopol 940, Carbopol 941 and Carbopol 980. An example of a suitable copolymer of a carboxylic acid containing a monomer and acrylic acid esters is Carbopol 1342. All Carbopol (trade mark) materials are available  
25 from Goodrich.

Suitable cross-linked polymers of acrylic acid and acrylate esters are Pemulen TR1 or Pemulen TR2. A suitable heteropolysaccharide gum is xanthan gum, for example that  
30 available as Kelzan mu.

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## COMPOSITIONS MADE WITH A CONDITIONING AGENT

Compositions in accordance with this invention may also be formulated as conditioners for the treatment of hair typically after shampooing and subsequent rinsing. These compositions will require silicone PSAs and a conditioning agent.

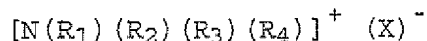
## Conditioning Agents

Such a conditioner will comprise at least one silicone pressure sensitive adhesive and one or more conditioning agents that are cosmetically acceptable and suitable for topical application to the hair.

Suitable conditioning agents are selected from cationic surfactants, used singly or in admixture.

Cationic surfactants useful in compositions of the invention contain amino or quaternary ammonium hydrophilic moieties which are positively charged when dissolved in the aqueous composition of the present invention.

Examples of suitable cationic surfactants are those corresponding to the formula:



in which  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  are independently selected from

(a) an aliphatic group of from 1 to 22 carbon atoms, or (b)

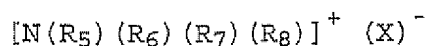
- 14 -

an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to 22 carbon atoms; and X is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate nitrate, sulphate, and alkylsulphate radicals.

The aliphatic groups can contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those of about 12 carbons, or higher, can be saturated or unsaturated.

The most preferred cationic surfactants for conditioner compositions of the present invention are monoalkyl quaternary ammonium compounds in which the alkyl chain length is C8 to C14.

Suitable examples of such materials correspond to the formula:



in which R<sub>5</sub> is a hydrocarbyl chain having 8 to 14 carbon atoms or a functionalized hydrocarbyl chain with 8 to 14 carbon atoms and containing ether, ester, amido or amino moieties present as substituents or as linkages in the radical chain, and R<sub>6</sub>, R<sub>7</sub> and R<sub>8</sub> are independently selected from (a) hydrocarbyl chains of from 1 to about 4 carbon atoms, or (b) functionalized hydrocarbyl chains having from 1 to about 4

- 15 -

carbon atoms and containing one or more aromatic, ether, ester, amido or amino moieties present as substituents or as linkages in the radical chain, and X is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate nitrate, sulphate, and alkylsulphate radicals.

The functionalised hydrocarbyl chains (b) may suitably contain one or more hydrophilic moieties selected from alkoxy (preferably C<sub>1</sub>-C<sub>3</sub> alkoxy), polyoxyalkylene (preferably C<sub>1</sub>-C<sub>3</sub> polyoxyalkylene), alkylamido, hydroxyalkyl, alkylester, and combinations thereof.

Preferably the hydrocarbyl chains R<sub>1</sub> have 12 to 14 carbon atoms, most preferably 12 carbon atoms. They may be derived from source oils which contain substantial amounts of fatty acids having the desired hydrocarbyl chain length. For example, the fatty acids from palm kernel oil or coconut oil can be used as a source of C<sub>8</sub> to C<sub>12</sub> hydrocarbyl chains.

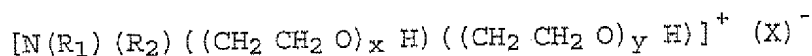
Typical monoalkyl quaternary ammonium compounds of the above general formula for use in shampoo compositions of the invention include:

(i) lauryl trimethylammonium chloride (available commercially as Arquad C35 ex-Akzo); cocodimethyl benzyl ammonium chloride (available commercially as Arquad DMCB-80 ex-Akzo)

(ii) compounds of the formula:

30

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wherein:

5     $x + y$  is an integer from 2 to 20;

$R_1$  is a hydrocarbyl chain having 8 to 14, preferably 12 to 14, most preferably 12 carbon atoms or a functionalised hydrocarbyl chain with 8 to 14, preferably 12 to 14, most  
10 preferably 12 carbon atoms and containing ether, ester, amido or amino moieties present as substituents or as linkages in the radical chain;

$R_2$  is a  $C_1$ - $C_3$  alkyl group or benzyl group, preferably methyl,  
15 and

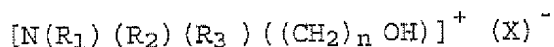
$X$  is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate nitrate, sulphate, methosulphate and  
20 alkylsulphate radicals.

Suitable examples are PEG- $n$  lauryl ammonium chlorides (where  $n$  is the PEG chain length), such as PEG-2 cocomonium chloride (available commercially as Ethoquad C12 ex-Akzo  
25 Nobel); PEG-2 cocobenzyl ammonium chloride (available commercially as Ethoquad CB/12 ex-Akzo Nobel); PEG-5 cocomonium methosulphate (available commercially as Rewoquat CPEM ex-Rewo); PEG-15 cocomonium chloride (available commercially as Ethoquad C/25 ex-Akzo)

30

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(iii) compounds of the formula:



5 wherein:

n is an integer from 1 to 4, preferably 2;

10 R<sub>1</sub> is a hydrocarbyl chain having 8 to 14, preferably 12 to 14, most preferably 12 carbon atoms;

R<sub>2</sub> and R<sub>3</sub> are independently selected from C<sub>1</sub> - C<sub>3</sub> alkyl groups, and are preferably methyl, and

15 X<sup>-</sup> is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate nitrate, sulphate, and alkylsulphate radicals.

20 Suitable examples are lauryldimethylhydroxyethylammonium chloride (available commercially as Prapagen HY ex-Clariant)

Mixtures of any of the foregoing cationic surfactants compounds may also be suitable.

25

Examples of suitable cationic surfactants include:

quaternary ammonium chlorides, e.g. alkyltrimethylammonium chlorides wherein the alkyl group has from about 8 to 22  
30 carbon atoms, for example octyltrimethylammonium chloride,

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dodecyltrimethylammonium chloride, hexadecyltrimethylammonium chloride, cetyltrimethylammonium chloride, octyldimethylbenzylammonium chloride, decyldimethylbenzylammonium chloride, stearyldi-  
5 methylbenzylammonium chloride, didodecyldimethylammonium chloride, dioctadecyldimethylammonium chloride, tallow trimethylammonium chloride, cocotrimethylammonium chloride, and the corresponding salts thereof, e.g., bromides, hydroxides. Cetylpyridinium chloride or salts thereof,  
10 e.g., chloride  
Quaternium -5  
Quaternium -31  
Quaternium -18  
and mixtures thereof.

15 In the conditioners of the invention, the level of cationic surfactant is preferably from 0.01 to 10, more preferably 0.05 to 5, most preferably 0.1 to 2 wt% of the total composition.

20 Optional Conditioning Materials

Fatty alcohol material

25 Conditioner compositions of the invention preferably additionally comprise a fatty alcohol material. The combined use of fatty alcohol materials and cationic surfactants in conditioning compositions is believed to be especially advantageous, because this leads to the formation of a  
30 lamellar phase, in which the cationic surfactant is dispersed.

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By "fatty alcohol material" is meant a fatty alcohol, an alkoxyated fatty alcohol, or a mixture thereof.

Representative fatty alcohols comprise from 8 to 22 carbon atoms, more preferably 16 to 20. Examples of suitable fatty alcohols include cetyl alcohol, stearyl alcohol and mixtures thereof. The use of these materials is also advantageous in that they contribute to the overall conditioning properties of compositions of the invention.

Alkoxyated, (e.g. ethoxyated or propoxyated) fatty alcohols having from about 12 to about 18 carbon atoms in the alkyl chain can be used in place of, or in addition to, the fatty alcohols themselves. Suitable examples include ethylene glycol cetyl ether, polyoxyethylene (2) stearyl ether, polyoxyethylene (4) cetyl ether, and mixtures thereof.

The level of fatty alcohol material in conditioners of the invention is suitably from 0.01 to 15, preferably from 0.1 to 10, and more preferably from 0.1 to 5 wt%. The weight ratio of cationic surfactant to fatty alcohol is suitably from 10:1 to 1:10, preferably from 4:1 to 1:8, optimally from 1:1 to 1:7, for example 1:3.

#### Cationic Polymers

Conditioner compositions of the invention can also contain a cationic polymer. Suitable cationic polymers are described hereinbelow in relation to shampoo compositions.



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# COMPOSITIONS MADE WITH A HAIR CLEANSING AGENT (SHAMPOO COMPOSITIONS)

A particularly preferred hair treatment composition in  
5 accordance with the invention is a shampoo composition that  
comprises of at least one silicone PSA and at least one  
cleansing agent.

Such a shampoo composition will comprise at least one  
10 silicone pressure sensitive adhesive and one or more  
cleansing surfactants which are cosmetically acceptable and  
suitable for topical application to the hair. Further  
surfactants may be present as an additional ingredient if  
sufficient for cleansing purposes is not provided as  
15 emulsifier for the silicone component. It is preferred that  
shampoo compositions of the invention comprise at least one  
further surfactant (in addition to that used as emulsifying  
agent for the silicone component) to provide a cleansing  
benefit.

20 Suitable cleansing agents, which may be used singularly or in  
combination, are selected from anionic, nonionic, amphoteric  
and zwitterionic surfactants, and mixtures thereof. The  
cleansing agent may be the same surfactant as the  
25 emulsifier, or may be different.

## CLEANSING AGENTS

Anionic cleansing surfactant  
30

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Shampoo compositions according to the invention will typically comprise one or more anionic cleansing surfactants which are cosmetically acceptable and suitable for topical application to the hair.

5

Examples of suitable anionic cleansing surfactants are the alkyl sulphates, alkyl ether sulphates, alkaryl sulphonates, alkanoyl isethionates, alkyl succinates, alkyl sulphosuccinates, N-alkyl sarcosinates, alkyl phosphates, alkyl ether phosphates, alkyl ether carboxylates, and alpha-olefin sulphonates, especially their sodium, magnesium, ammonium and mono-, di- and triethanolamine salts. The alkyl and acyl groups generally contain from 8 to 18 carbon atoms and may be unsaturated. The alkyl ether sulphates, alkyl ether phosphates and alkyl ether carboxylates may contain from 1 to 10 ethylene oxide or propylene oxide units per molecule.

Typical anionic cleansing surfactants for use in shampoo compositions of the invention include sodium oleyl succinate, ammonium lauryl sulphosuccinate, ammonium lauryl sulphate, sodium dodecylbenzene sulphonate, triethanolamine dodecylbenzene sulphonate, sodium cocoyl isethionate, sodium lauryl isethionate and sodium N-lauryl sarcosinate. The most preferred anionic surfactants are sodium lauryl sulphate, sodium lauryl ether sulphate(n)EO, (where n ranges from 1 to 3), ammonium lauryl sulphate and ammonium lauryl ether sulphate(n)EO, (where n ranges from 1 to 3).

Mixtures of any of the foregoing anionic cleansing surfactants may also be suitable.

30

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The total amount of anionic cleansing surfactant in shampoo compositions of the invention is generally from 5 to 30, preferably from 6 to 20, more preferably from 8 to 16 wt%.

#### 5 Amphoteric Surfactants

The shampoo composition can include other cleansing agents, to help impart aesthetic, physical or cleansing properties to the composition.

10

A preferred example is an amphoteric or zwitterionic surfactant, which can be included in an amount ranging from 0 to about 8, preferably from 1 to 4 wt%.

15 Examples of amphoteric and zwitterionic surfactants include alkyl amine oxides, alkyl betaines, alkyl amidopropyl betaines, alkyl sulphobetaines (sultaines), alkyl glycinate, alkyl carboxyglycinates, alkyl amphopropionates, alkylamphoglycinates, alkyl amidopropyl hydroxysultaines,  
20 acyl taurates and acyl glutamates, wherein the alkyl and acyl groups have from 8 to 19 carbon atoms. Typical amphoteric and zwitterionic surfactants for use in shampoos of the invention include lauryl amine oxide, cocodimethyl sulphopropyl betaine and preferably lauryl betaine,  
25 cocamidopropyl betaine and sodium cocamphopropionate.

#### Nonionic Surfactants

Another preferred example is a nonionic surfactant, which can  
30 be included in an amount ranging from 0 to 8, preferably from 2 to 5 wt%.

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For example, representative nonionic surfactants that can be included in shampoo compositions of the invention include condensation products of aliphatic (C<sub>8</sub>-C<sub>18</sub>) primary or secondary linear or branched chain alcohols or phenols with alkylene oxides, usually ethylene oxide and generally having from 6 to 30 ethylene oxide groups.

Other representative nonionic surfactants include mono- or di-alkyl alkanolamides. Examples include coco mono- or di-ethanolamide and coco mono-isopropanolamide.

Further nonionic surfactants which can be included in shampoo compositions of the invention are the alkyl polyglycosides (APGs). Typically, the APG is one which comprises an alkyl group connected (optionally via a bridging group) to a block of one or more glycosyl groups. Preferred APGs are defined by the following formula:



wherein R is a branched or straight chain alkyl group which may be saturated or unsaturated and G is a saccharide group.

R may represent a mean alkyl chain length of from about C<sub>5</sub> to about C<sub>20</sub>. Preferably R represents a mean alkyl chain length of from about C<sub>8</sub> to about C<sub>12</sub>. Most preferably the value of R lies between about 9.5 and about 10.5. G may be selected from C<sub>5</sub> or C<sub>6</sub> monosaccharide residues, and is preferably a glucoside. G may be selected from the group comprising

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glucose, xylose, lactose, fructose, mannose and derivatives thereof. Preferably G is glucose.

5 The degree of polymerization, n, may have a value of from about 1 to about 10 or more. Preferably, the value of n lies in the range of from about 1.1 to about 2. Most preferably the value of n lies in the range of from about 1.3 to about 1.5.

10 Suitable alkyl polyglycosides for use in the invention are commercially available and include for example those materials identified as: Oramix NS10 ex Seppic; Plantaren 1200 and Plantaren 2000 ex Henkel.

15 Other sugar-derived nonionic surfactants which can be included in shampoo compositions of the invention include the C<sub>10</sub>-C<sub>18</sub> N-alkyl (C<sub>1</sub>-C<sub>6</sub>) polyhydroxy fatty acid amides, such as the C<sub>12</sub>-C<sub>18</sub> N-methyl glucamides, as described for example in WO 92 06154 and US 5 194 639, and the N-alkoxy polyhydroxy  
20 fatty acid amides, such as C<sub>10</sub>-C<sub>18</sub> N-(3-methoxypropyl) glucamide.

#### OPTIONAL SHAMPOO INGREDIENTS

##### 25 Cationic Surfactants

The shampoo composition can also optionally include one or more cationic co-surfactants included in an amount ranging from 0.01 to 10, more preferably from 0.05 to 5, most  
30 preferably from 0.05 to 2 wt%. Useful cationic surfactants

- 25 -

are described hereinabove in relation to conditioner compositions.

The total amount of surfactant (including any co-surfactant,  
5 and/or any emulsifier) in shampoo compositions of the invention is generally from 5 to 50, preferably from 5 to

#### Cationic Polymer

- 10 A cationic polymer is a preferred ingredient in shampoo compositions of the invention, for enhancing conditioning performance of the shampoo.

The cationic polymer may be a homopolymer or be formed from two or more types of monomers. The molecular weight of the polymer will generally be between 5 000 and 10,000,000, typically at least 10 000 and preferably in the range 100 000 to about 2,000,000. The polymers will have cationic nitrogen containing groups such as quaternary ammonium or protonated amino groups, or a mixture thereof.

The cationic nitrogen-containing group will generally be present as a substituent on a fraction of the total monomer units of the cationic polymer. Thus when the polymer is not a homopolymer it can contain spacer non-cationic monomer units. Such polymers are described in the CTFA Cosmetic Ingredient Directory, 3rd edition. The ratio of the cationic to non-cationic monomer units is selected to give a polymer having a cationic charge density in the required range.

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Suitable cationic conditioning polymers include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as (meth)acrylamide, alkyl and dialkyl (meth)acrylamides, alkyl (meth)acrylate, vinyl caprolactone and vinyl pyrrolidine. The alkyl and dialkyl substituted monomers preferably have C1-C7 alkyl groups, more preferably C1-3 alkyl groups. Other suitable spacers include vinyl esters, vinyl alcohol, maleic anhydride, propylene glycol and ethylene glycol.

The cationic amines can be primary, secondary or tertiary amines, depending upon the particular species and the pH of the composition. In general secondary and tertiary amines, especially tertiary, are preferred.

Amine substituted vinyl monomers and amines can be polymerized in the amine form and then converted to ammonium by quaternization.

The cationic conditioning polymers can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

Suitable cationic conditioning polymers include, for example:

- copolymers of 1-vinyl-2-pyrrolidine and 1-vinyl-3-methyl-imidazolium salt (e.g. chloride salt), referred to in the industry by the Cosmetic, Toiletry, and

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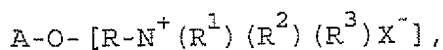
- Fragrance Association, (CTFA) as Polyquaternium-16. This material is commercially available from BASF Wyandotte Corp. (Parsippany, NJ, USA) under the LUVIQUAT tradename (e.g. LUVIQUAT FC 370);
- copolymers of 1-vinyl-2-pyrrolidine and dimethylaminoethyl methacrylate, referred to in the industry (CTFA) as Polyquaternium-11. This material is available commercially from Gaf Corporation (Wayne, NJ, USA) under the GAFQUAT tradename (e.g., GAFQUAT 755N);
  - cationic diallyl quaternary ammonium-containing polymers including, for example, dimethyldiallylammonium chloride homopolymer and copolymers of acrylamide and dimethyldiallylammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively;
  - mineral acid salts of amino-alkyl esters of homo- and copolymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, (as described in U.S. Patent 4,009,256);
  - cationic polyacrylamides (as described in WO95/22311).

Other cationic conditioning polymers that can be used include cationic polysaccharide polymers, such as cationic cellulose derivatives, cationic starch derivatives, and cationic guar gum derivatives. Suitably, such cationic polysaccharide polymers have a charge density in the range from 0.1 to 4 meq/g.



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Cationic polysaccharide polymers suitable for use in compositions of the invention include those of the formula:



wherein: A is an anhydroglucose residual group, such as a starch or cellulose anhydroglucose residual. R is an alkylene, oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof.  $R^1$ ,  $R^2$  and  $R^3$  independently represent alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms. The total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in  $R^1$ ,  $R^2$  and  $R^3$ ) is preferably about 20 or less, and  $X^-$  is an anionic counterion.

Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR (trade mark) and LR (trade mark) series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10. Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. (Edison, NJ, USA) under the tradename Polymer LM-200.

Other suitable cationic polysaccharide polymers include quaternary nitrogen-containing cellulose ethers (e.g. as

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described in U.S. Patent 3,962,418), and copolymers of etherified cellulose and starch (e.g. as described in U.S. Patent 3,958,581).

A particularly suitable type of cationic polysaccharide polymer that can be used is a cationic guar gum derivative, such as guar hydroxypropyltrimonium chloride (commercially available from Rhone-Poulenc in their JAGUAR trademark series).

Examples are JAGUAR C13S, which has a low degree of substitution of the cationic groups and high viscosity. JAGUAR C15, having a moderate degree of substitution and a low viscosity, JAGUAR C17 (high degree of substitution, high viscosity), JAGUAR C16, which is a hydroxypropylated cationic guar derivative containing a low level of substituent groups as well as cationic quaternary ammonium groups, and JAGUAR 162 which is a high transparency, medium viscosity guar having a low degree of substitution.

Preferably the cationic conditioning polymer is selected from cationic cellulose and cationic guar derivatives.

Particularly preferred cationic polymers are JAGUAR C13S, JAGUAR C15, JAGUAR C17 and JAGUAR C16 and JAGUAR C162.

The cationic conditioning polymer will generally be present in compositions of the invention at levels of from 0.01 to 5, preferably from 0.05 to 1, more preferably from 0.08 to 0.5

5 wt%.

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### Conditioning Agents

The compositions of this invention can also contain one or more conditioning agents selected from silicone conditioning agents and non-silicone oily conditioning agents.

When conditioning agent is present in the hair treatment compositions in droplet form, the droplets may be liquid, semi-solid or solid in nature, so long as they are substantially uniformly dispersed in the fully formulated product. Any droplets of oily conditioning agent are preferably present as either liquid or semi-solid droplets, more preferably as liquid droplets.

### 15 Silicone conditioning agents

The compositions of the invention can contain, emulsified droplets of a silicone conditioning agent, for enhancing conditioning performance. The silicone conditioning agent is insoluble in the aqueous matrix of the composition and so is present in an emulsified form, with the silicone present as dispersed droplets.

Suitable silicone conditioning agents include polydiorganosiloxanes, in particular polydimethylsiloxanes which have the CTFA designation dimethicone. Also suitable for use compositions of the invention (particularly shampoos and conditioners) are polydimethyl siloxanes having hydroxyl end groups, which have the CTFA designation dimethiconol. Also suitable for use in compositions of the invention are silicone gums having a slight degree of cross-linking, as

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are described for example in WO 96/31188. These materials can impart body, volume and stylability to hair, as well as good wet and dry conditioning.

- 5 The viscosity of the emulsified silicone conditioning agent itself (not the emulsion or the final hair conditioning composition) is typically at least 10,000 cst. In general we have found that conditioning performance increases with increased viscosity. Accordingly, the viscosity of the
- 10 silicone conditioning agent itself is preferably at least 60,000 cst, most preferably at least 500,000 cst, ideally at least 1,000,000 cst. Preferably the viscosity does not exceed  $10^9$  cst for ease of formulation.
- 15 Emulsified silicone conditioning agents for use in the shampoo compositions of the invention will typically have an average silicone droplet size in the composition of less than 30, preferably less than 20, more preferably less than 10  $\mu\text{m}$ . We have found that reducing the droplet size
- 20 generally improves conditioning performance. Most preferably the average silicone droplet size of the emulsified silicone in the composition is less than 2  $\mu\text{m}$ , ideally it ranges from 0.01 to 1  $\mu\text{m}$ . Silicone emulsions having an average silicone droplet size of  $\leq 0.15 \mu\text{m}$  are
- 25 generally termed microemulsions.

Suitable silicone emulsions for use in the invention are also commercially available in a pre-emulsified form.

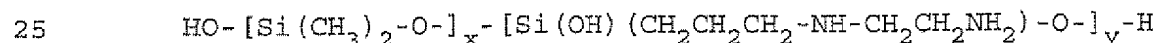
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Examples of suitable pre-formed emulsions include emulsions DC2-1766, DC2-1784, and microemulsions DC2-1865 and DC2-1870, all available from Dow Corning. These are all emulsions/microemulsions of dimethiconol. Cross-linked silicone gums are also available in a pre-emulsified form, which is advantageous for ease of formulation. A preferred example is the material available from Dow Corning as DC 2-1787, which is an emulsion of cross-linked dimethiconol gum. A further preferred example is the material available from Dow Corning as DC 2-1391, which is a microemulsion of cross-linked dimethiconol gum.

A further preferred class of silicone conditioning agents for inclusion in shampoos and conditioners of the invention are amino functional silicones. By "amino functional silicone" is meant a silicone containing at least one primary, secondary or tertiary amine group, or a quaternary ammonium group.

Examples of suitable amino functional silicones include:

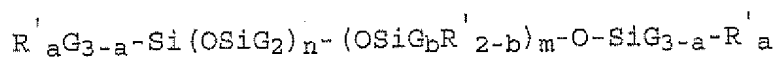
- (i) polysiloxanes having the CTFA designation "amodimethicone", and the general formula:



wherein x and y are numbers such that the molecular weight is between about 5,000 and 500,000.

- (ii) polysiloxanes having the formula:

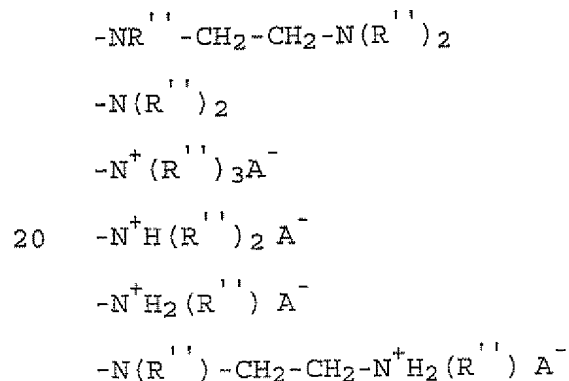
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in which:

- 5 G is selected from H, phenyl, OH or C<sub>1-8</sub> alkyl, e.g. methyl;  
 a is 0 or an integer from 1 to 3, preferably 0;  
 b is 0 or 1, preferably 1;  
 m and n are numbers such that (m + n) can range from 1 to  
 2000, preferably from 50 to 150;  
 10 m is a number from 1 to 2000, preferably from 1 to 10;  
 n is a number from 0 to 1999, preferably from 49 to 149, and

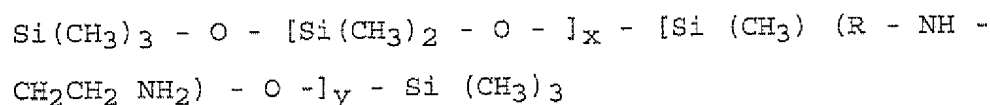
R' is a monovalent radical of formula -C<sub>q</sub>H<sub>2q</sub>L in which q is a  
 number from 2 to 8 and L is an aminofunctional group selected  
 15 from the following:



in which R'' is selected from H, phenyl, benzyl, or a  
 25 saturated monovalent hydrocarbon radical, e.g. C<sub>1-20</sub> alkyl,  
 and A<sup>-</sup> is a halide ion, e.g. chloride or bromide.

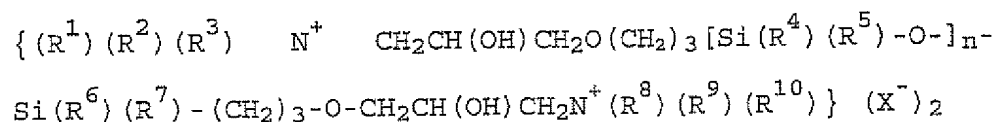
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Suitable amino functional silicones corresponding to the above formula include those polysiloxanes termed "trimethylsilylamodimethicone" as depicted below, and which are sufficiently water insoluble so as to be useful in compositions of the invention:



wherein  $x + y$  is a number from about 50 to about 500, and wherein R is an alkylene group having from 2 to 5 carbon atoms. Preferably, the number  $x + y$  is in the range of from about 100 to about 300.

(iii) quaternary silicone polymers having the general formula:



wherein  $\text{R}^1$  and  $\text{R}^{10}$  may be the same or different and may be independently selected from H, saturated or unsaturated long or short chain alk(en)yl, branched chain alk(en)yl and  $\text{C}_5$ - $\text{C}_8$  cyclic ring systems;

$\text{R}^2$  through  $\text{R}^9$  may be the same or different and may be independently selected from H, straight or branched chain lower alk(en)yl, and  $\text{C}_5$ - $\text{C}_8$  cyclic ring systems;

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n is a number within the range of about 60 to about 120, preferably about 80, and

X<sup>-</sup> is preferably acetate, but may instead be for example halide, organic carboxylate, organic sulphonate or the like. Suitable quaternary silicone polymers of this class are described in EP-A-0 530 974.

Amino functional silicones suitable for use in shampoos and conditioners of the invention will typically have a mole % amine functionality in the range of from about 0.1 to about 8.0 mole %, preferably from about 0.1 to about 5.0 mole %, most preferably from about 0.1 to about 2.0 mole %. In general the amine concentration should not exceed about 8.0 mole % since we have found that too high an amine concentration can be detrimental to total silicone deposition and therefore conditioning performance.

The viscosity of the amino functional silicone is not particularly critical and can suitably range from about 100 to about 500,000 cSt.

Specific examples of amino functional silicones suitable for use in the invention are the aminosilicone oils DC2-8220, DC2-8166, DC2-8466, and DC2-8950-114 (all ex Dow Corning), and GE 1149-75, (ex General Electric Silicones).

Also suitable are emulsions of amino functional silicone oils with non ionic and/or cationic surfactant.



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Suitably such pre-formed emulsions will have an average amino functional silicone droplet size in the shampoo composition of less than 30, preferably less than 20, more preferably less than 10  $\mu\text{m}$ . Again, we have found that  
5 reducing the droplet size generally improves conditioning performance. Most preferably the average amino functional silicone droplet size in the composition is less than 2  $\mu\text{m}$  ideally it ranges from 0.01 to 1  $\mu\text{m}$ .

10 Pre-formed emulsions of amino functional silicone are also available from suppliers of silicone oils such as Dow Corning and General Electric. Specific examples include DC929 Cationic Emulsion, DC939 Cationic Emulsion, and the non-ionic emulsions DC2-7224, DC2-8467, DC2-8177 and DC2-  
15 8154 (all ex Dow Corning).

An example of a quaternary silicone polymer useful in the present invention is the material K3474, ex Goldschmidt.

20 For shampoo compositions according to the invention intended for the treatment of "mixed" hair (i.e. greasy roots and dry ends), it is particularly preferred to use a combination of amino functional and non-amino functional silicone in compositions of the invention, especially when these are in  
25 the form of shampoo compositions. In such a case, the weight ratio of amino functional silicone to non-amino functional silicone will typically range from 1:2 to 1:20, preferably 1:3 to 1:20, more preferably 1:3 to 1:8. The total amount of silicone incorporated into compositions  
30 of the invention depends on the level of conditioning desired and the material used. A preferred amount is from

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0.01 to 10 wt% although these limits are not absolute. The lower limit is determined by the minimum level to achieve conditioning and the upper limit by the maximum level to avoid making the hair and/or skin unacceptably greasy.

5

We have found that a total amount of silicone of from 0.3 to 5, preferably 0.5 to 3 wt% is a suitable level.

10 The viscosity of silicones and silicone emulsions can be measured by means of a glass capillary viscometer as set out further in Dow Corning Corporate Test Method CTM004, July 20 1970.

15 In compositions comprising silicone conditioning agent, it is preferred that a suspending agent for the silicone conditioning agent also be present. Suitable suspending agents are as described hereinabove.

Non-silicone oily conditioning components

20

Compositions according to the present invention may also comprise a dispersed, non-volatile, water-insoluble oily conditioning agent.

25 This component will be dispersed in the composition in the form of droplets, which form a separate, discontinuous phase from the aqueous, continuous phase of the composition. In other words, the oily conditioning agent will be present in the shampoo composition in the form of an oil-in-water  
30 emulsion.

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Suitably, the  $D_{3,2}$  average droplet size of the oily conditioning component is at least 0.4, preferably at least 0.8, and more preferably at least 1  $\mu\text{m}$ . Additionally, the  $D_{3,2}$  average droplet size of the oily conditioning component is preferably no greater than 10, more preferably no greater than 8, more preferably no greater than 5, yet more preferably no greater than 4, and most preferably no greater than 3.5  $\mu\text{m}$ .

The oily conditioning agent may suitably be selected from oily or fatty materials, and mixtures thereof.

Oily or fatty materials are preferred conditioning agents in the shampoo compositions of the invention for adding shine to the hair and also enhancing dry combing and dry hair feel.

Preferred oily and fatty materials will generally have a viscosity of less than 5 Pa.s, more preferably less than 1 Pa.s, and most preferably less than 0.5 Pa.s, e.g. 0.1 Pa.s and under as measured at 25°C with a Brookfield Viscometer (e.g. Brookfield RV) using spindle 3 operating at 100 rpm.

Oily and fatty materials with higher viscosities may be used. For example, materials with viscosities as high as 65 Pa.s may be used. The viscosity of such materials (i.e. materials with viscosities of 5 Pa.s and greater) can be measured by means of a glass capillary viscometer as set out further in Dow Corning Corporate Test Method CTM004, July 20 1970.

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Suitable oily or fatty materials are selected from hydrocarbon oils, fatty esters and mixtures thereof.

Hydrocarbon oils include cyclic hydrocarbons, straight chain  
5 aliphatic hydrocarbons (saturated or unsaturated), and  
branched chain aliphatic hydrocarbons (saturated or  
unsaturated). Straight chain hydrocarbon oils will  
preferably contain from about 12 to about 30 carbon atoms.  
Branched chain hydrocarbon oils can and typically may  
10 contain higher numbers of carbon atoms. Also suitable are  
polymeric hydrocarbons of alkenyl monomers, such as  $C_2-C_6$   
alkenyl monomers. These polymers can be straight or  
branched chain polymers. The straight chain polymers will  
typically be relatively short in length, having a total  
15 number of carbon atoms as described above for straight chain  
hydrocarbons in general. The branched chain polymers can  
have substantially higher chain length. The number average  
molecular weight of such materials can vary widely, but will  
typically be up to about 2000, preferably from about 200 to  
20 about 1000, more preferably from about 300 to about 600.

Specific examples of suitable hydrocarbon oils include  
paraffin oil, mineral oil, saturated and unsaturated  
dodecane, saturated and unsaturated tridecane, saturated and  
25 unsaturated tetradecane, saturated and unsaturated  
pentadecane, saturated and unsaturated hexadecane, and  
mixtures thereof. Branched-chain isomers of these  
compounds, as well as of higher chain length hydrocarbons,  
can also be used. Exemplary branched-chain isomers are  
30 highly branched saturated or unsaturated alkanes, such as  
the permethyl-substituted isomers, e.g., the permethyl-

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substituted isomers of hexadecane and eicosane, such as 2, 2, 4, 4, 6, 6, 8, 8-dimethyl-10-methylundecane and 2, 2, 4, 4, 6, 6-dimethyl-8-methylnonane, sold by Permethyl Corporation. A further example of a hydrocarbon polymer is  
5 polybutene, such as the copolymer of isobutylene and butene. A commercially available material of this type is L-14 polybutene from Amoco Chemical Co. (Chicago, Ill., U.S.A.).

Particularly preferred hydrocarbon oils are the various  
10 grades of mineral oils. Mineral oils are clear oily liquids obtained from petroleum oil, from which waxes have been removed, and the more volatile fractions removed by distillation. The fraction distilling between 250°C to 300°C is termed mineral oil, and it consists of a mixture of  
15 hydrocarbons ranging from  $C_{16}H_{34}$  to  $C_{21}H_{44}$ . Suitable commercially available materials of this type include Sirius M85 and Sirius M125, all available from Silkolene.

Suitable fatty esters are characterized by having at least  
20 10 carbon atoms, and include esters with hydrocarbyl chains derived from fatty acids or alcohols, e.g., monocarboxylic acid esters, polyhydric alcohol esters, and di- and tricarboxylic acid esters. The hydrocarbyl radicals of the fatty esters hereof can also include or have covalently  
25 bonded thereto other compatible functionalities, such as amides and alkoxy moieties, such as ethoxy or ether linkages.

Monocarboxylic acid esters include esters of alcohols and/or  
30 acids of the formula  $R'COOR$  in which  $R'$  and  $R$  independently

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denote alkyl or alkenyl radicals and the sum of carbon atoms in R' and R is at least 10, preferably at least 20.

Specific examples include, for example, alkyl and alkenyl  
5 esters of fatty acids having aliphatic chains with from  
about 10 to about 22 carbon atoms, and alkyl and/or alkenyl  
fatty alcohol carboxylic acid esters having an alkyl and/or  
alkenyl alcohol-derived aliphatic chain with about 10 to  
about 22 carbon atoms, benzoate esters of fatty alcohols  
10 having from about 12 to 20 carbon atoms.

The monocarboxylic acid ester need not necessarily contain  
at least one chain with at least 10 carbon atoms, so long as  
the total number of aliphatic chain carbon atoms is at least  
15 10. Examples include isopropyl isostearate, hexyl laurate,  
isohexyl laurate, isohexyl palmitate, isopropyl palmitate,  
decyl oleate, isodecyl oleate, hexadecyl stearate, decyl  
stearate, isopropyl isostearate, dihexyldecyl adipate,  
lauryl lactate, myristyl lactate, cetyl lactate, oleyl  
20 stearate, oleyl oleate, oleyl myristate, lauryl acetate,  
cetyl propionate, and oleyl adipate.

Di- and trialkyl and alkenyl esters of carboxylic acids can  
also be used. These include, for example, esters of C<sub>4</sub>-C<sub>8</sub>  
25 dicarboxylic acids such as C<sub>1</sub>-C<sub>22</sub> esters (preferably C<sub>1</sub>-C<sub>6</sub>)  
of succinic acid, glutaric acid, adipic acid, hexanoic acid,  
heptanoic acid, and octanoic acid. Examples include  
diisopropyl adipate, diisohexyl adipate, and diisopropyl  
sebacate. Other specific examples include isocetyl stearyl  
30 stearate, and tristearyl citrate.

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Polyhydric alcohol esters include alkylene glycol esters, for example ethylene glycol mono and di-fatty acid esters, diethylene glycol mono- and di-fatty acid esters, polyethylene glycol mono- and di-fatty acid esters, 5 propylene glycol mono- and di-fatty acid esters, polypropylene glycol monooleate, polypropylene glycol monostearate, ethoxylated propylene glycol monostearate, polyglycerol poly-fatty acid esters, ethoxylated glyceryl monostearate, 1,3-butylene glycol monostearate, 1,3-butylene 10 glycol distearate, polyoxyethylene polyol fatty acid ester, sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters and mono-, di-and triglycerides.

Particularly preferred fatty esters are mono-, di- and 15 triglycerides, more specifically the mono-, di-, and tri-esters of glycerol and long chain carboxylic acids such as C<sub>1</sub>-C<sub>22</sub> carboxylic acids. A variety of these types of materials can be obtained from vegetable and animal fats and oils, such as coconut oil, castor oil, safflower oil, 20 sunflower oil, cottonseed oil, corn oil, olive oil, cod liver oil, almond oil, avocado oil, palm oil, sesame oil, peanut oil, lanolin and soybean oil. Synthetic oils include triolein and tristearin glyceryl dilaurate.

25 Specific examples of preferred materials include cocoa butter, palm stearin, sunflower oil, soyabean oil and coconut oil.

The oily or fatty material is suitably present at a level of 30 from 0.05 to 10, preferably from 0.2 to 5, more preferably from about 0.5 to 3 wt%.

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The compositions of this invention preferably contain no more than 3 wt% of a styling polymer, more preferably less than 1% of a styling polymer, preferably contain less than 0.1% by weight a styling polymer, and optimally are free of styling polymer.

In hair treatment compositions containing a conditioning agent, it is preferred that a cationic polymer also be present.

10

#### Adjuvants

The compositions of the present invention may also contain adjuvants suitable for hair care. Generally such ingredients are included individually at a level of up to 2, preferably up to 1 wt% of the total composition.

Among suitable hair care adjuvants, are:

- (i) natural hair root nutrients, such as amino acids and sugars. Examples of suitable amino acids include arginine, cysteine, glutamine, glutamic acid, isoleucine, leucine, methionine, serine and valine, and/or precursors and derivatives thereof. The amino acids may be added singly, in mixtures, or in the form of peptides, e.g. di- and tripeptides. The amino acids may also be added in the form of a protein hydrolysate, such as a keratin or collagen hydrolysate. Suitable sugars are glucose, dextrose and fructose. These may be added singly or in the form of, e.g. fruit extracts. A particularly preferred combination of natural hair root nutrients for inclusion in compositions of



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the invention is isoleucine and glucose. A particularly preferred amino acid nutrient is arginine.

(ii) hair fibre benefit agents. Examples are:

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- ceramides, for moisturizing the fibre and maintaining cuticle integrity. Ceramides are available by extraction from natural sources, or as synthetic ceramides and pseudoceramides. A preferred ceramide is Ceramide II, ex  
10 Quest. Mixtures of ceramides may also be suitable, such as Ceramides LS, ex Laboratoires Serobiologiques.

The invention will now be further illustrated by the following, non-limiting Examples.

Table 1

Ingredient	Example 1 Weight %	Example 2 Weight %	Example 3 Weight %	Example 4 Weight %	Example 5 Weight %	Example 6 Weight %
Stearamidopropyl dimethylamine,	0.750	0.750	0.750	0.750	0.750	0.750
PEG-2 oleamonium chloride & propylene glycol	2.000	2.000	2.000	2.000	2.000	2.000
Behentrimonium Methosulfate and cetearyl alcohol	0.25	1.000	1.000	1.000	1.000	1.000
Cetyl alcohol	3.000	3.000	3.000	3.000	3.000	3.000
Stearyl alcohol	2.000	2.000	2.000	2.000	2.000	2.000
Disodium EDTA	0.100	0.100	0.100	0.100	0.100	0.100
Dimethiconol	0.000	0.000	0.000	0.000	0.8	0.000
Silicone Fluid 245	0.000	0.000	0.000	0.000	2.000	0.000
Fragrance	0.600	0.600	0.600	0.600	0.600	0.600
Low Tack Silicone PSA emulsion <sup>1</sup>	0.000	0.2	0.4	0.4	0.000	0.000
Colloidal silica	0.5	0.000	0.000	0.000	0.000	0.000
Water, fragrance, preservatives	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
Total	100.00	100.00	100.00	100.00	100.00	100.00

<sup>1</sup> Low Tack Silicone PSA emulsion is available from Dow Corning Corp. (DC 5-7300)

which is a 40% emulsion of silicone PSA that contains 65% silicone resin and 35% silicone polymer.

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Table 2:

	Example 7	Example 8	Example 9	Example 10	Example 11
Ingredient	Weight %	Weight %	Weight %	Weight %	Weight %
Water, soft	45.000	45.000	45.000	45.000	45.000
Hydroxyethylcellulose	0.200	0.000	0.000	0.000	0.200
Cetrimonium Chloride	2.800	2.500	2.500	2.500	2.800
Quaternium-18 and propylene glycol	0.500	0.400	0.400	0.400	0.500
Cetyl/Stearyl alcohol	3.000	3.000	3.000	3.000	3.000
Disodium EDTA, 100% active	0.100	0.100	0.100	0.100	0.100
Dimethiconol	0.8	0.6	0.6	0.6	0.8
Silicone fluid 245	0.000	0.000	0.000	0.000	0.000
Fragrance	0.400	0.400	0.600	0.600	0.600
Low Tack Silicone PSA emulsion <sup>1</sup>	0.000	0.000	0.000	0.500	0.000
Water, Fragrance, Preservative	q.s.	q.s.	q.s.	q.s.	q.s.
Total	100.000	100.000	100.000	100.000	100.000

5

Measurement of Static and Dynamic friction:

Friction measurements are performed using a modified version of a previously described methodology based on Dynamic Mechanical Analysis (DMA) (Ref: US Patent No. 5,968,286 which is hereby incorporated by reference). Testing involves the application of different force profiles to a bundle of hair fibers. One manner for carrying out testing involves using a single cantilever geometry wherein only one side of a hair bundle is secured. The extent to which the bundle deflects under force will possess a dependance on the

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interfiber friction. As such, relative differences in the frictional properties of hair can be measured by comparing the results from treated and untreated hair bundles. A diagram of the experimental set up is shown below in Figure

5 1.

Two-gram hair tresses are prepared using natural brown hair purchased from Imhair Ltd.(Italy). Before testing, all tresses are cleaned thoroughly using standard surfactant  
10 solutions. Each tress is cut to the length of 6 inches. Testing is performed with the hair encased in a thin-walled latex tube with an inside diameter of 3 mm, and outside diameter 3.4 mm. A close up of the hair and the tube is shown in Figure 2.

15

For statistical purposes, 4 tube samples are tested for each formulation. Testing is first performed on an untreated hair array. After testing, the hair is removed from the latex tube and treated with the test formula. The formula is  
20 applied in the proportion 0.2 ml to 2 g of hair for a shampoo, and 0.3 ml to 2 g of hair for a conditioner product. Each hair array is treated for 1 minute and then rinsed for 30 seconds in warm water (40°C), at a flow rate of 2 l/min. After treatment the arrays are air dried for 24  
25 hours at 30% RH, and a temperature of 20°C. The samples are then placed back in the latex tube and equilibrated for the next 24 hours under the same conditions. The treated hair arrays are then tested again to allow for differences in deflection to be observed as a result of surface  
30 modification imparted by the test material.

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A Perkin Elmer DMA 7e housed within an environmentally controlled chamber is used for all our measurements. The tube sample is mounted in the single cantilever DMA fixture in such a way that the length of the latex tube protruding from the clamp is 20 mm (see Fig.1). The instrument probe imposes a bending force on the top of the tube at a distance of 7.5 mm from the clamp.

By imposing different force profiles, it is possible to measure different frictional properties of the hair. For example, a measure of the static friction can be obtained by performing a test in which the bending force is gradually increased. Meanwhile, the dynamic friction is measured by imposing an oscillating sinusoidal force. In each case, the instrument measures the resulting deflection or strain that results in the specimen. More detailed information regarding these two modes of operation are given below.

#### Change in static friction

The coefficient of static friction is calculated from a test in which an increasing bending force deflects the tube sample. Initially, the process is elastic and consequently a linear relationship exists between the stress (force/unit area) and the deflection. Under these conditions the array behaves like a solid rod, since the interfiber friction and the external pressure of the tube holds the fibers together and prevents movement of the individual fibers. However, at a certain critical force, adjacent fibers will start to slide over one another. As the result of this interfiber slip, the total resistance of the sample towards the bending

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force decreases. From this point on, the deflection increases faster than the bending stress. That is, the linear relationship between the stress and strain is lost. The critical deflection  $d_c$  at which the interfiber slip appears is measured by the instrument and can be used to calculate an average coefficient of internal static friction in the tube sample. The change in static friction is calculated by comparing the critical deflection of the same hair array before and after treatment with the test sample.

10

#### Change in dynamic friction

The dynamic friction test is somewhat more complex. The use of an oscillating force allows for the deconvolution of a material's elastic (storage) and viscous (lost) components. These quantities identify the ability of the material to recover from deformation (elasticity) or to dissipate a portion of the mechanical energy (damping). Friction is a property that is associated with the dissipation of the mechanical energy and therefore can be probed using the loss component that is obtained from a dynamic mechanical test.

Dynamic friction testing is performed by introducing a gradually increasing dynamic force to the sample at a constant frequency. Furthermore, this dynamic force is superimposed over a gradually increasing static force. This behavior is shown schematically in Figure. 3.

Calculation of the coefficient of dynamic friction is more complex and requires a detailed analysis involving the movement of the fiber bundle as a result of the two

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- 50 -

superimposed bending forces. As the magnitude of both the static and dynamic force is raised, so the magnitude of the deflection also increases. That is, the amplitude of dynamic bending also increases. Furthermore, the magnitude of the bending amplitude is influenced by the surface frictional properties of the hair fibers. The measurement of the amplitude before and after the treatment allows for assessment of a relative change in dynamic friction  $\Delta fd$ .

The relative coefficient of dynamic friction is calculated by:

$$\Delta fd/fd = (A_U - A_T)/A_U$$

where  $A_U$  is the maximum amplitude of bending before treatment, and  $A_T$  is the maximum amplitude for the same hair array after the treatment.

If the same hair array were treated with a conditioning formula that reduces the surface friction, then the same bending force would be able to generate longer interfiber slip and the higher amplitude of bending (Fig. 4). The results of frictional tests are valid only for the treatments, which do not change the bulk properties of hair fibers, but only their surface friction.

The experimental data below demonstrates the beneficial properties of compositions of the invention.

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Table 3 includes the static and dynamic friction properties as measured by the above mentioned DMA technique for the formulation examples as listed in tables 1 and 2.

5

Table 3

Conditioner Description	Static Friction (%)	Dynamic Friction (%)
Example 1	210	280
Example 2	17	3
Example 3	31	5
Example 4	45	26
Example 5	30	2
Example 6	-21	-29
Example 7	-10	-31
Example 8	25	-11
Example 9	-17.67	-22.67
Example 10	24	25
Example 11	-16	-29

#### Shampoo compositions:

The invention will now be further illustrated by the following, non-limiting example 12 of a shampoo formulation.

10

Table 4

Ingredient	Example 12 Weight %	Example 13 Weight %
Emulsion stabilizer	0.400	0.400
Ammonium Lauryl Sulphate	7.605	7.605
Ammonium Laureth Sulphate	5.941	5.941
Cocamide MEA	1.300	1.300
PEG-6 Cocamide	0.650	0.650
Propylene Glycol	0.500	0.500
Guar Hydroxypropyltrimonium chloride	0.100	0.100
Dimethiconol	1.000	1.000
Low Tack Silicone PSA <sup>1</sup>	0.000	0.750
Chelating agent	0.080	0.080
Water, Fragrance, and Preservatives	q.s.	q.s.



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Table 5 includes the static and dynamic friction properties as measured by the above mentioned DMA technique for the formulation examples as listed in tables 4.

5

Table 5

Shampoo Description	Static Friction (%)	Dynamic Friction (%)
Example 12	-7	-11
Example 13	18	3

Suspension Composition:

- 10 The invention will now be further illustrated by the following, non-limiting examples of a suspension.

Example 13	
Description	Wt. %
Silicone PSA emulsion (40% active)	2.00
Carbopol 980, 100% active	1.00
DMDM Hydantion	0.1
Kathon CG, 39% active	0.04
Soft water, 100% active	96.86
Total	100.00

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CLAIMS

1. An aqueous hair treatment composition comprising:
  - a) at least one silicone pressure sensitive adhesive;
  - 5 and
  - b) at least one material selected from the group consisting of:
    - i) a hair conditioning agent,
    - ii) a hair cleansing agent, and
    - 10 iii) an agent for suspending said silicone pressure sensitive adhesive in a manner which enables said silicone pressure sensitive adhesive to be deposited on said hair.
- 15 2. An aqueous hair treatment composition according to claim 1 wherein said composition increases static friction of dry hair by at least about 10%, and wherein said composition increases dynamic friction of dry hair by no more than about 100% or decreases or leaves unchanged  
20 said dynamic friction.
3. An aqueous hair treatment composition according to claim 2 wherein said composition increases dynamic friction of dry hair by no more than about 60%.
- 25 4. An aqueous hair treatment composition according to claim 2 wherein said composition increases dynamic friction of dry hair by no more than about 40%.

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5. An aqueous hair treatment composition according to claim 2 wherein said composition increases static friction of dry hair by at least about 15%.
- 5 6. An aqueous hair treatment composition according to claim 2 wherein said composition increases static friction of dry hair by at least about 20%.
- 10 7. A composition in accordance with claim 1, wherein said silicone pressure sensitive adhesive is the product of mixing 30 to 60 parts by weight of a silanol-terminated polydiorganosiloxane of Tg below -20°C and viscosity 0.1-30000 Pa.s at 25°C lightly crosslinked with 40 to 70 parts by weight of a silanol-containing silicone resin  
15 of Tg above 0°C comprising monovalent trihydrocarbonsiloxy (M) groups of the formula  $R''_3SiO_{1/2}$  and tetrafunctional (Q) groups  $SiO_{4/2}$  wherein  $R''$  denotes a monovalent hydrocarbon group having 1 to 6 carbon atoms, the number ratio of M groups to Q groups being in  
20 the range 0.5:1 to 1.2:1.
8. A composition in accordance to claim 1, wherein said pressure sensitive adhesive is dispersed as an emulsion comprising a disperse silicone phase emulsified in a  
25 continuous water phase in the presence of a surfactant, wherein the disperse silicone phase comprises 40 to 80 % by weight of a silicone pressure sensitive adhesive, which is the lightly crosslinked product of mixing a silanol-terminated polydiorganosiloxane of Tg below -  
30 20°C with a silanol-containing silicone resin of Tg

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above 0°C, dispersed in 60 to 20 % by weight of a volatile silicone fluid having a boiling point below 300°C, the emulsion being substantially free of any non-silicon-containing volatile organic material.

5

9. An aqueous hair treatment composition according to claim 1 comprising:

- 10 a) about 0.01% to about 10% of at least one silicone pressure sensitive adhesive; and
- b1) about 0.01% to about 10% of at least one suspending agent; or
- b2) about 0.05% to about 10% of at least one hair conditioning agent; or
- 15 b3) about 5% to about 40% of at least one hair cleansing agent.

10. An aqueous hair treatment composition according to claim 8 comprising:

20

- a) about 0.05% to about 5% of at least one silicone pressure sensitive adhesive; and
- b1) about 0.1% to about 5% of at least one suspending agent; or
- 25 b2) about 0.1% to about 5% of at least one hair conditioning agent; or
- b3) about 10% to about 20% of at least one hair cleansing agent.

30 11. An aqueous hair treatment composition according to claim 1 which is a leave-in composition.

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12. An aqueous hair treatment composition according to claim 1 which is a rinse-out composition.
13. A composition according to claim 1 which is a hair  
5 conditioner and which comprises a conditioning agent selected from the group consisting of :  
octyltrimethylammonium chloride,  
dodecyltrimethylammonium chloride,  
hexadecyltrimethylammonium chloride,  
10 cetyltrimethylammonium chloride,  
octyldimethylbenzylammonium chloride,  
decyldimethylbenzylammonium chloride, stearyldi-  
methylbenzylammonium chloride, didodecyldimethylammonium  
chloride, dioctadecyldimethylammonium chloride, tallow  
15 trimethylammonium chloride, cocotrimethylammonium  
chloride, Cetylpyridinium chloride, Quaternium -5  
Quaternium -31 Quaternium -18;  
and mixtures thereof.
- 20 14. A composition in accordance with claim 1 which comprises  
a suspending agent selected from the group consisting of  
polyacrylic acids, cross-linked polymers of acrylic  
acid, copolymers of acrylic acid with a hydrophobic  
monomer, copolymers of carboxylic acid-containing  
25 monomers and acrylic esters, cross-linked copolymers of  
acrylic acid and acrylate esters, heteropolysaccharide  
gum; ethylene glycol stearate, alkanolamides of fatty  
acids ; ethylene glycol distearate; polyethylene glycol  
3 distearate; Carbopol 420, Carbopol 488; Carbopol 493;  
30 Carbopol 910, Carbopol 934, Carbopol 940, Carbopol 941;  
Carbopol 980; Carbopol 1342; cross-linked polymers of

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acrylic acid and acrylate ester , xanthan gum, and mixtures thereof

- 5 15. A composition in accordance with claim 1 which is a shampoo and which comprises a hair cleansing agent selected from the group consisting of an anionic surfactant, a non-ionic surfactant, an amphoteric surfactant, and mixtures thereof.
- 10 16. A composition in accordance with claim 14 wherein said hair cleansing agent is selected from the group consisting of sodium dodecylbenzene sulphonate, sodium, lauryl sulphate, sodium lauryl ether sulphate nEO, where n is from 1 to 20; octylphenol ether sulphate nEO where  
15 n is from 1 to 20, sodium dioctylsulphosuccinate; nonylphenol ethoxylate nEO, where n is from 1 to 50, alcohol ethoxylates; lauryl alcohol nEO, where n is from 1 to 50, polyoxyethylene monostearate where the number of oxyethylene units is from 1 to 30.
- 20 17. A composition in accordance with claim 1, which comprises a conditioning agent selected from the group consisting of a volatile silicone, a nonvolatile silicone, and mixtures thereof .
- 25 18. A method for providing hair with body which comprises contacting said hair with a composition in accordance with claim 1.

Fig.1.

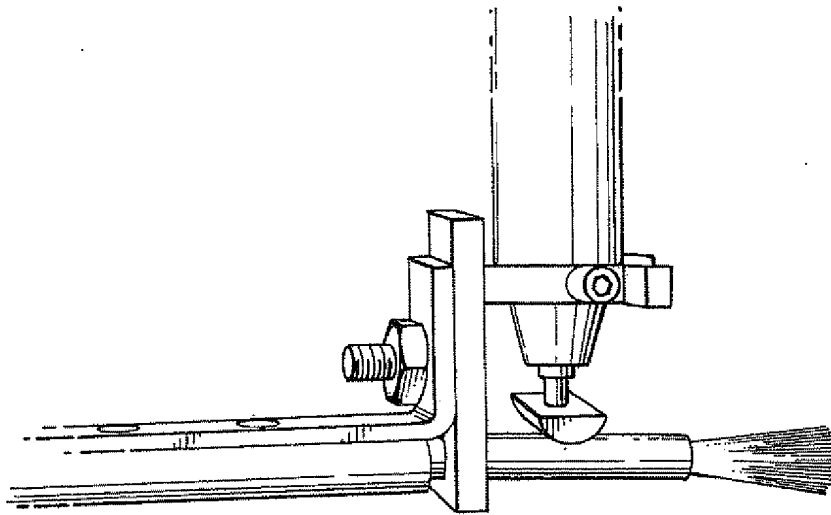
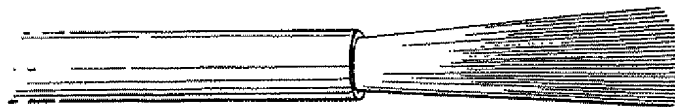


Fig.2.



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Fig.3.

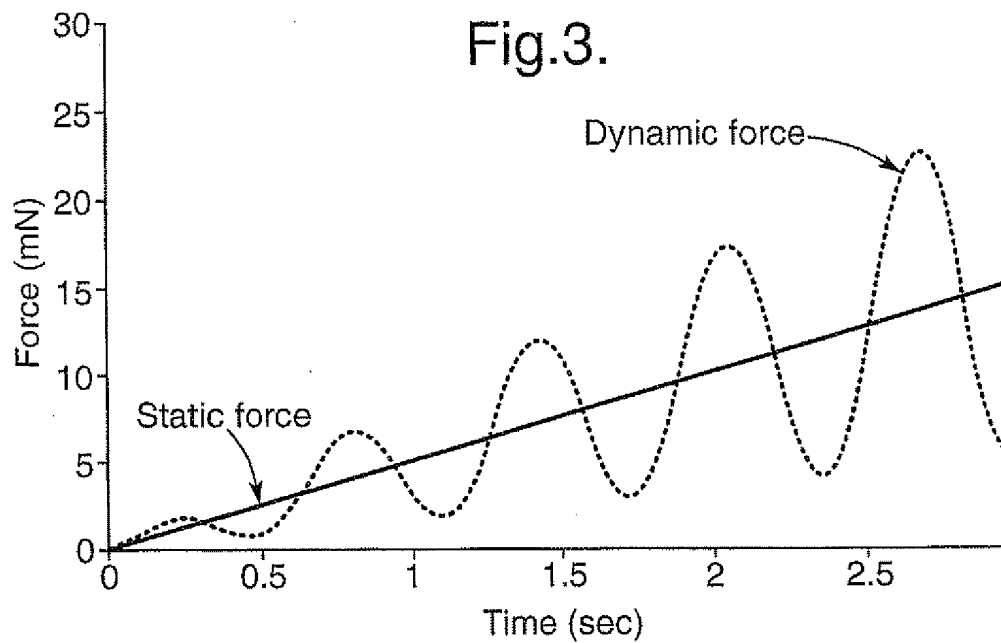
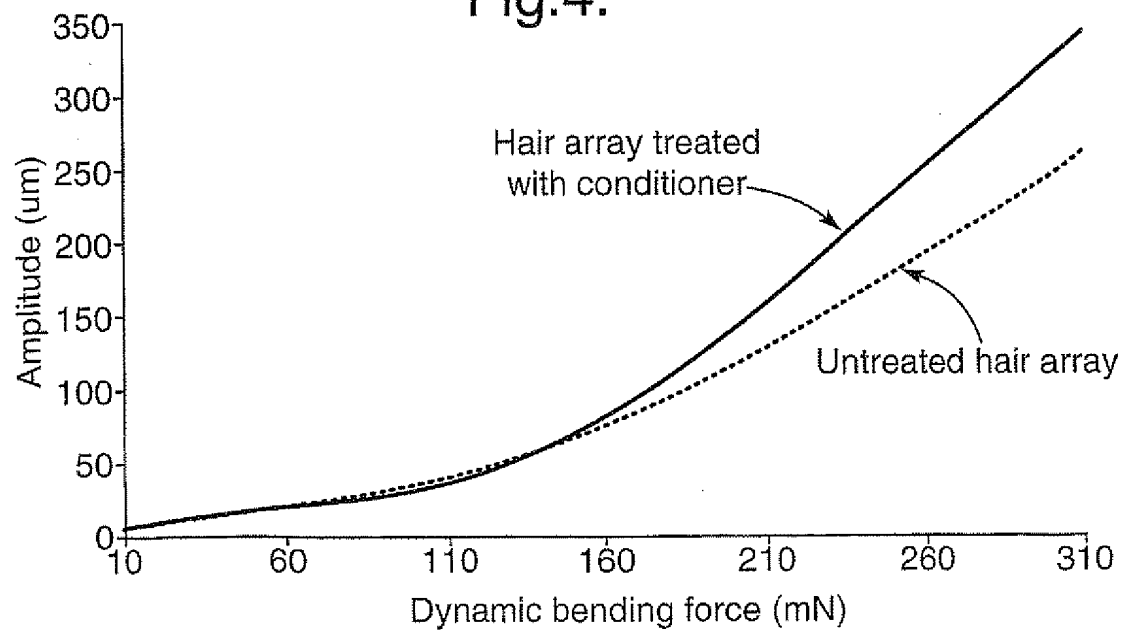


Fig.4.





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According to International Patent Classification (IPC) or to both national classification and IPC

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

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## HAIR TREATMENT COMPOSITIONS

### FIELD OF THE INVENTION

5

This invention relates to leave on hair treatment compositions and to their use in the treatment of hair.

### BACKGROUND AND PRIOR ART

10

One of the most common methods for styling hair has been applying fixative agents to the hair, such as high molecular weight polymers. The problem with using such fixative agents is that they have a tendency to make the hair feel sticky, stiff and crisp. Furthermore conventional fixative agents also tend to make consumers hands feel sticky when they are applying or styling their hair with compositions containing them.

15

20 One way in which this problem has been addressed in the past has been to include conditioning agents, for example silicones and cationic surfactants, in the compositions, to counter the negative effects of the styling agents.

25

Although such conditioning agents do provide substantial improvements in for example the wet and dry combing properties of the hair and in the smoothness of the hair, they tend to have a negative effect on the styling of hair e.g. poor style creation and hold. Furthermore the use of conditioners does not overcome the sticky feeling on

30

consumers hands during application and styling with the product.

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The present invention provides high styling efficacy (e. g. control, ease of styling, style longevity and manageability) without undue stiffness and sticky feel.

- 5 Pressure sensitive adhesives (PSAs) have been used in hair care compositions as described in US5166276, EP408311, EP412707 and EP412704. However these PSAs tend to hydrolyse in aqueous and hydroalcoholic hair care products.
- 10 The present invention has the added advantage that hair can be styled without the consumers hands becoming sticky.

- A further advantage is that hair styled with compositions of the present invention does not become limp or lose its style
- 15 or curl retention in humid conditions.

The invention also relates to PSAs which are particularly stable in aqueous and hydroalcoholic hair care products.

20

#### **SUMMARY OF THE INVENTION**

- Accordingly, this invention provides a mousse, cream, lotion, tonic or spray leave on hair treatment composition
- 25 comprising a silicone pressure sensitive adhesive present as an emulsion.

- This invention provides for the use of silicone PSA's as defined herein in a hair treatment composition to impart
- 30 styling without compromising feel, especially omitting stickiness, on hair and hands.

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A method for styling hair is also described which comprises contacting the hair with the composition described above.

## 5 DETAILED DESCRIPTION OF THE INVENTION

Unless specified otherwise, all wt% values quoted hereinafter are percentages by weight based on total weight of the hair treatment composition.

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By "insoluble" is meant that the material is not soluble in water (distilled or equivalent) at a concentration of 0.1%, at 25°C.

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### Silicone Pressure Sensitive Adhesives

This present invention relates to the use of silicone PSAs for hair care applications.

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The term "silicone pressure sensitive adhesive" (SPSA) refers to pressure sensitive adhesives comprising a silicone resin and a polydiorganosiloxane. These "pressure sensitive adhesive" (PSA) materials are permanently tacky at room temperature and able to develop measurable adhesion to a surface simply upon contact or by the application of a light pressure. Generally they do not require heat. No chemical reaction takes place between the adhesive and the adherent, no curing of the adhesive is necessary and no solvent is required to be lost during the adhesion process.

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In the context of the present invention there are 3 types of silicone PSAs:

i) One class of silicone pressure sensitive adhesives consists of a mixture of (i) a silanol end-blocked polydiorganosiloxane fluid, e.g. a polydimethylsiloxane polymer and (ii) a trimethylsilyl end-blocked polysilicate resin such as a silicate resin consisting of a benzene-soluble resinous copolymer containing silicon-bonded hydroxyl radicals and consisting essentially of triorganosiloxy units of the formula  $R_3SiO_{1/2}$  and tetrafunctionalsiloxy units of the formula  $SiO_{4/2}$  in a ratio of about 0.6 to 0.9 triorganosiloxy units for each tetrafunctionalsiloxy unit present in the copolymer, wherein each R is a monovalent organic radical independently selected from the group consisting of hydrocarbon radicals of from 1 to 6 inclusive carbon atoms. U.S. Patent No. 2,736, 721 to Dexter et al. and U.S. Patent No. 2,814,601 to Currie et al. teach such or similar silicone pressure sensitive adhesives.

ii) A preferred class of silicone PSAs are prepared by condensing the silicone fluid and the silicate. In this preferred condensation reaction, the silicate resin and the silicone fluid are mixed together in the presence of a catalytic amount of a silanol condensation catalyst and then the silicate resin and the silicone fluid are condensed, for example, by heating under reflux conditions for 1 to 20 hours. Examples of silanol condensation catalysts are primary, secondary and tertiary amines, carboxylic acids of these amines and quaternary ammonium salts.



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- iii) A further optional step can also employ an alkenyl-functional polymer and a crosslinking agent containing silicone-bonded hydrogen atoms, they are cured by a hydrosilation addition reaction using a platinum-type catalyst as described in US-4988779. In such systems the molar ratio of silicon bonded hydrogen groups to silicone bonded alkenyl groups is typically greater than 1. However these systems are not highly preferred.
- 10 A preferred silicone PSA comprises (a) 40 to 70 parts by weight of at least one silicone copolymer resin and (b) 30 to 60 parts by weight of at least one polydiorganosiloxane. The silanol content of the silicone pressure sensitive adhesive composition is reduced by chemically treating at least a portion of (a), (b) or the mixture of (a) and (b) with at least one chemical treating agent (c) that reacts with silicon-bonded hydroxyl groups to reduce the silicon-bonded hydroxyl content of the composition.
- 20 Preferably the silicon-bonded hydroxyl content of the composition is reduced to a range of between 8000 and 13,000.
- The silicone resin copolymers (i) usually contain silicon-bonded hydroxyl radicals in amounts which typically range from about 1 to 4 weight percent of silicon-bonded hydroxyl radicals and comprise triorganosiloxy units of the formula  $R_3SiO_{1/2}$  and tetrafunctional siloxy units of the formula  $SiO_{4/2}$  in a mole ratio of from 0.6 to 0.9  $R_3Si_{1/2}$  units for each  $SiO_{4/2}$  unit present. Blends of two or more such copolymers may also be used. There should be at least some

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and preferably at least 0.5% silicon-bonded hydroxyl content to enable the polydiorganosiloxane component to copolymerize with the copolymer resin and/or to react with the end blocking agent being added to chemically treat the silicone pressure-sensitive adhesive composition. Each R denotes, independently, a monovalent hydrocarbon radical having from 1 to 6 inclusive carbon atoms such as methyl, ethyl, propyl, isopropyl, hexyl, cyclohexyl, vinyl, allyl, propenyl and phenyl. Preferably, the  $R_3SiO_{1/2}$  units are  $Me_3SiO_{1/2}$  units and/or  $Me_2R_1SiO_{1/2}$  units wherein  $R_1$  is a vinyl ("Vi") or phenyl ("Ph") radical. More preferably, no more than 10 mole percent of the  $R_3SiO_{1/2}$  units present in resin copolymer (i) are  $Me_2R_2SiO_{1/2}$  units and the remaining units are  $Me_3SiO_{1/2}$  units where each  $R_2$  is a vinyl radical. Most preferably, the  $R_3SiO_{1/2}$  units are  $Me_3SiO_{1/2}$  units.

The preferred class of silicone PSAs (ii) usually comprise one or more polydiorganosiloxanes comprising  $ARSiO$  units terminated with endblocking  $TRASiO_{1/2}$  units, where each R is as defined in the paragraph above. Each A radical is selected from radicals such as R or halohydro-carbon radicals of from 1 to 6 inclusive carbon atoms such as chloromethyl, chloropropyl, 1-chloro-2-methylpropyl, 3,3,3-trifluoropropyl and  $F_3C(CH_2)_5$  radicals. Thus the polydiorganosiloxane can contain  $Me_2SiO$  units,  $PhMeSiO$  units,  $MeViSiO$  units,  $Ph_2SiO$  units, methylethylsiloxyl units, 3,3,3-trifluoropropyl units and 1-chloro, 2-methylpropyl units and the like. Preferably, the  $ARSiO$  units are selected from the group consisting of  $R_2SiO$ ,  $RR'SiO$  units,  $Ph_2SiO$  units and combinations of both where R and R'

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are as for R in the paragraph above, at least 50 mole percent of the R' radicals present in the polydiorganosiloxane (ii) are methyl radicals and no more than 50 mole percent of the total moles of ARSiO units present in each polydiorganosiloxane of (ii) are Ph<sub>2</sub>SiO units. More preferably, no more than 10 mole percent of the ARSiO units present in each polydiorganosiloxane (ii) are MeRSiO units where R is as above defined and the remaining ARSiO units present in each polydiorganosiloxane are Me<sub>2</sub>SiO units. Most preferably, substantially all of the ARSiO units are Me<sub>2</sub>SiO units. Each T radical is R, OH, H or OR' radicals where each R' is an alkyl radical of from 1 to 4 inclusive carbon atoms such as methyl, ethyl, n-propyl, and isobutyl radicals. H, OH and OR' provide a site for reaction with the endblocking triorganosilyl units of ingredient (iii) and also provide a site for condensation with other such radicals on polydiorganosiloxanes (ii) or with the silicon-bonded hydroxyl groups present in resin copolymer (i). Use of polydiorganosiloxanes where T is OH is most preferred because the polydiorganosiloxane (ii) can then readily copolymerize with the resin copolymer (i). When an appropriate catalyst such as HCl, which is generated when chlorosilanes are used, or ammonia, which is generated when organosilazanes are used, as endblocking agents, then triorganosiloxy (e.g., R<sub>3</sub>SiO<sup>1/2</sup> such as (CH<sub>3</sub>)<sub>3</sub>SiO<sup>1/2</sup> or CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>SiO<sup>1/2</sup>) unit terminated polydiorganosiloxanes can be employed because some of the triorganosiloxy units can be cleaved when the condensation reaction is conducted with heating. The cleavage exposes a silicon-bonded hydroxyl radical which can then condense with silicon-bonded hydroxyl radicals in the copolymer resin,

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with endblocking triorganosilyl units or with other polydiorganosiloxanes containing H, OH or OR' radicals or silicon-bonded hydroxyl radicals exposed by cleavage reactions. Mixtures of polydiorganosiloxanes containing  
5 different substituent radicals may also be used.

Each of the polydiorganosiloxanes (ii) preferably have a viscosity of from 100 centipoise to 30,000,000 centipoise at  
10 25° C. (100 millipascal- seconds to 30,000 pascal seconds (Pa.s) where 1 centipoise equals 1 millipascal second). As is well-known, viscosity is directly related to the average number of diorganosiloxane units present for a series of polydiorganosiloxanes of varying molecular weights which  
15 have the same endblocking units. Polydiorganosiloxanes having a viscosity of from about 100 to 100,000 centipoise at 25° C. range from fluids to somewhat viscous polymers. These polydiorganosiloxanes are preferably pre-reacted with resin copolymer (i) prior to condensation in the presence of  
20 endblocking agent (iii) to improve the tack and adhesion properties of the resulting PSA as will be further described. Polydiorganosiloxanes having viscosities in excess of 100,000 centipoise can typically be subjected to the condensation/endblocking step (II) of the present  
25 invention without pre-reaction. Polydiorganosiloxanes having viscosities in excess of 1,000, 000 centipoise are highly viscous products often referred to as gums and the viscosity is often expressed in terms of a Williams Plasticity value (polydimethylsiloxane gums of about 10,000,000 centipoise  
30 viscosity typically have a Williams Plasticity Value of about 50 mils (1.27 mm) or more at 25° C.).

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Examples of endblocking agents (iii) are (Me<sub>3</sub>Si)<sub>2</sub>NH,  
 (ViMe<sub>2</sub>Si)<sub>2</sub>NH, (MePhViSi)<sub>2</sub>NH, (CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>Si)<sub>2</sub>NH,  
 (Me<sub>3</sub>Si)<sub>2</sub>NMe, (ClCH<sub>2</sub>Me<sub>2</sub>Si)<sub>2</sub>NH, Me<sub>3</sub>SiOMe, Me<sub>3</sub>SiOC<sub>2</sub>H<sub>5</sub>,  
 5 Ph<sub>3</sub>SiOC<sub>2</sub>H<sub>5</sub>, (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>SiOC<sub>2</sub>H<sub>5</sub>, Me<sub>2</sub>PhSiOC<sub>2</sub>H<sub>5</sub>, (i-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>SiOH,  
 Me<sub>3</sub>Si(OC<sub>3</sub>H<sub>7</sub>), MePhViSiOMe, Me<sub>3</sub>SiCl, Me<sub>2</sub>ViSiCl, MePhViSiCl,  
 (H<sub>2</sub>CCHCH<sub>2</sub>)Me<sub>2</sub>SiCl, (n-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>SiCl, (F<sub>3</sub>CCF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>SiCl,  
 NCCH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>SiCl, (n-C<sub>6</sub>H<sub>13</sub>)<sub>3</sub>SiCl, MePh<sub>2</sub>SiCl, Me<sub>3</sub>SiBr, (t-  
 C<sub>4</sub>H<sub>9</sub>)Me<sub>2</sub>SiCl, CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>SiCl, (Me<sub>3</sub>Si)<sub>2</sub>O, (Me<sub>2</sub>PhSi)<sub>2</sub>O,  
 10 BrCH<sub>2</sub>Me<sub>2</sub>SiOSiMe<sub>3</sub>, (p-FC<sub>6</sub>H<sub>4</sub>Me<sub>2</sub>Si)<sub>2</sub>O, (CH<sub>3</sub>COOCH<sub>2</sub>Me<sub>2</sub>Si)<sub>2</sub>O,  
 [(H<sub>2</sub>CCCH<sub>3</sub>COOCH<sub>2</sub>CH<sub>2</sub>)Me<sub>2</sub>Si]<sub>2</sub>O, [(CH<sub>3</sub>COOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Me<sub>2</sub>Si]<sub>2</sub>O,  
 [(C<sub>2</sub>H<sub>5</sub>OOCH<sub>2</sub>CH<sub>2</sub>)Me<sub>2</sub>Si]<sub>2</sub>O, [(H<sub>2</sub>CCHCOOCH<sub>2</sub>)Me<sub>2</sub>Si]<sub>2</sub>O, (Me<sub>3</sub>Si)<sub>2</sub>S,  
 (Me<sub>3</sub>Si)<sub>3</sub>N, Me<sub>3</sub>SiNHCONHSiMe<sub>3</sub>, F<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Me<sub>2</sub>SiNMeCOCH<sub>3</sub>,  
 (Me<sub>3</sub>Si)(C<sub>4</sub>H<sub>9</sub>)NCON(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, (Me<sub>3</sub>Si)PhNCONHPh, Me<sub>3</sub>SiNHMe,  
 15 Me<sub>3</sub>SiN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, Ph<sub>3</sub>SiNH<sub>2</sub>, Me<sub>3</sub>SiNHOCCH<sub>3</sub>, Me<sub>3</sub>SiOOCCH<sub>3</sub>,  
 [(CH<sub>3</sub>CONHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Me<sub>2</sub>Si]<sub>2</sub>O, Me<sub>3</sub>SiO(CH<sub>2</sub>)<sub>4</sub>OSiMe<sub>3</sub>,  
 Me<sub>3</sub>SiNHOCCH<sub>3</sub>, Me<sub>3</sub>SiCCH, HO(CH<sub>2</sub>)<sub>4</sub>Me<sub>2</sub>Si]<sub>2</sub>O,  
 (HOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>Me<sub>2</sub>Si)<sub>2</sub>O, H<sub>2</sub>N(CH<sub>2</sub>)<sub>3</sub>Me<sub>2</sub>SiOCH<sub>3</sub>,  
 CH<sub>3</sub>CH(CH<sub>2</sub>NH<sub>2</sub>)CH<sub>2</sub>Me<sub>2</sub>SiOCH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>NHCH<sub>2</sub>CH<sub>2</sub>S(CH<sub>2</sub>)<sub>6</sub>Me<sub>2</sub>SiOC<sub>2</sub>H<sub>5</sub>,  
 20 HSCH<sub>2</sub>CH<sub>2</sub>NH(CH<sub>2</sub>)<sub>4</sub>Me<sub>2</sub>SiOC<sub>2</sub>H<sub>5</sub>, HOCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>Me<sub>2</sub>SiOCH<sub>3</sub>.

Preferably, the endblocking agent employed is (Me<sub>3</sub>Si)<sub>2</sub>NH.

The PSAs described are emulsified.

25 A preferred silicone PSA emulsion can be prepared by mixing  
 the silicone PSA in suitable solvents to give a dispersed  
 phase. It is advantageous if this dispersed phase comprises  
 20 to 80 % by weight of the silicone pressure sensitive  
 adhesive. Preferably at least one solvent will be a  
 30 volatile solvent, meaning a solvent with a boiling point  
 below 300°C. One or more of the solvents is preferably a

- 10 -

silicone. The PSA/solvent mixture is optionally emulsified in water using one or more surfactants. The preferred surfactants are anionic or nonionic surfactants, especially a blend of anionic and nonionic surfactants. The silicone solvent can be a linear polydiorganosiloxane such as hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, dodecamethylpentasiloxane or a polydimethylsiloxane of viscosity 1cSt, or can be a cyclic siloxane such as decamethylcyclopentasiloxane or octamethylcyclotetrasiloxane or can be a mixture of one or more linear polydimethylsiloxanes with one or more cyclic siloxanes. Other solvents include ethyl acetate and hydrocarbons (e.g heptane, hexane, isododecane).

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#### Hair Styling Polymer

The compositions of the invention may further comprise from 0.001% to 10% by weight of a hair styling polymer. More preferred amounts of hair styling polymer in the compositions of the invention are from 0.1% to 5% by weight of the composition, even more preferably from 0.5% to 3% by weight. However it is highly preferable if additional hair styling polymer they are not present or present in levels below 0.01 wt% of the total composition.

Hair styling polymers are well known. Suitable hair styling polymers include commercially available polymers that contain moieties that render the polymers cationic, anionic, amphoteric or nonionic in nature. Suitable hair styling

polymers include, for example, block and graft copolymers. The polymers may be synthetic or naturally derived.

Examples of anionic hair styling polymers are:

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copolymers of vinyl acetate and crotonic acid; terpolymers of vinyl acetate, crotonic acid and a vinyl ester of an alpha-branched saturated aliphatic monocarboxylic acid such as vinyl neodecanoate;

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copolymers of methyl vinyl ether and maleic anhydride (molar ratio about 1:1) wherein such copolymers are 50% esterified with a saturated alcohol containing from 1 to 4 carbon atoms such as ethanol or butanol;

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acrylic copolymers containing acrylic acid or methacrylic acid as the anionic radical-containing moiety with other monomers such as: esters of acrylic or methacrylic acid with one or more saturated alcohols having from 1 to 22 carbon atoms (such as methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-butyl acrylate, t-butyl acrylate, t-butyl methacrylate, n-butyl methacrylate, n-hexyl acrylate, n-octyl acrylate, lauryl methacrylate and behenyl acrylate); glycols having from 1 to 6 carbon atoms (such as

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hydroxypropyl methacrylate and hydroxyethyl acrylate); styrene; vinyl caprolactam; vinyl acetate; acrylamide; alkyl acrylamides and methacrylamides having 1 to 8 carbon atoms in the alkyl group (such as methacrylamide, t-butyl acrylamide and n-octyl acrylamide); and other compatible

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unsaturated monomers.

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The additional styling polymer may also contain grafted silicone, such as polydimethylsiloxane.

Specific examples of suitable anionic hair styling polymers  
5 are:

RESYN® 28-2930 available from National Starch (vinyl acetate/crotonic acid/vinyl neodecanoate copolymer);

10 ULTRAHOLD® 8 available from BASF (CTFA designation Acrylates/acrylamide copolymer);

the GANTREZ®ES series available from ISP Corporation esterified copolymers of methyl vinyl ether and maleic  
15 anhydride);

Luviset PUR® available from BASF.

Other suitable anionic hair styling polymers include  
20 carboxylated polyurethanes. Carboxylated polyurethane resins are linear, hydroxyl-terminated copolymers having pendant carboxyl groups. They may be ethoxylated and/or propoxylated at least at one terminal end. The carboxyl group can be a carboxylic acid group or an ester group,  
25 wherein the alkyl moiety of the ester group contains one to three carbon atoms. The carboxylated polyurethane resin can also be a copolymer of polyvinylpyrrolidone and a polyurethane, having a CTFA designation PVP/polycarbamyl polyglycol ester. Suitable carboxylated polyurethane resins  
30 are disclosed in EP-A-0619111 and US Patent No. 5,000,955.



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Other suitable hydrophilic polyurethanes are disclosed in US Patent Nos. 3,822,238; 4,156,066; 4,156,067; 4,255,550; and 4,743,673.

- 5 Amphoteric hair styling polymers which can contain cationic groups derived from monomers such as t-butyl aminoethyl methacrylate as well as carboxyl groups derived from monomers such as acrylic acid or methacrylic acid can also be used in the present invention. One specific example of
- 10 an amphoteric hair styling polymer is Amphomer® (Octylacrylamide/ acrylates/butylaminoethyl methacrylate copolymer) sold by the National Starch and Chemical Corporation.
- 15 Examples of nonionic hair styling polymers are homopolymers of N- vinylpyrrolidone and copolymers of N-vinylpyrrolidone with compatible nonionic monomers such as vinyl acetate. Nonionic polymers containing N- vinylpyrrolidone in various weight average molecular weights are available commercially
- 20 from ISP Corporation - specific examples of such materials are homopolymers of N-vinylpyrrolidone having an average molecular weight of about 630,000 sold under the name PVP K-90 and are homopolymers of N-vinylpyrrolidone having an average molecular weight of about 1,000,000 sold under the
- 25 name of PVP K-120.

Other suitable nonionic hair styling polymers are cross-linked silicone resins or gums. Specific examples include rigid silicone polymers such as those described in EP-A-

30 0240350 and cross-linked silicone gums such as those described in WO 96/31188.

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Examples of cationic hair styling polymers are copolymers of amino-functional acrylate monomers such as lower alkyl aminoalkyl acrylate, or methacrylate monomers such as  
5 dimethylaminoethyl methacrylate, with compatible monomers such as N-vinylpyrrolidone, vinyl caprolactam, alkyl methacrylates (such as methyl methacrylate and ethyl methacrylate) and alkyl acrylates (such as ethyl acrylate and n-butyl acrylate).

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Specific examples of suitable cationic polymers are:

copolymers of N-vinylpyrrolidone and dimethylaminoethyl methacrylate, available from ISP Corporation as Copolymer  
15 845, Copolymer 937 and Copolymer 958;

copolymers of N-vinylpyrrolidone and dimethylaminopropylacrylamide or methacrylamide, available from ISP Corporation as Styleze® CC10;

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copolymers of N-vinylpyrrolidine and dimethylaminoethyl methacrylate;

copolymers of vinylcaprolactam, N-vinylpyrrolidone and  
25 dimethylaminoethylmethacrylate;

Polyquaternium-4 (a copolymer of diallyldimonium chloride and hydroxyethylcellulose);

30 Polyquaternium-11 (formed by the reaction of diethyl sulphate and a copolymer of vinyl pyrrolidone and dimethyl

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aminoethylmethacrylate), available from ISP as Gafquat® 734, 755 and 755N, and from BASF as Luviquat® PQ11;

Polyquaternium-16 (formed from methylvinylimidazolium  
5 chloride and vinylpyrrolidone), available from BASF as  
Luviquat® FC 370, FC 550, FC 905 and HM-552;

Polyquaternium-46 (prepared by the reaction of  
vinylcaprolactam and vinylpyrrolidone with  
10 methylvinylimidazolium methosulphate), available from BASF  
as Luviquat®Hold.

Examples of suitable naturally-derived polymers include  
shellac, alginates, gelatins, pectins, cellulose derivatives  
15 and chitosan or salts and derivatives thereof. Commercially  
available examples include Kytamer® (ex Amerchol) and Amaze®  
(ex National Starch).

Also suitable for use as additional styling polymers in the  
20 compositions of the invention are the ionic copolymers  
described in WO 93/03703, the polysiloxane-grafted polymers  
disclosed in WO 93/23446, the silicone-containing  
polycarboxylic acid copolymers described in WO 95/00106 or  
WO 95/32703, the thermoplastic elastomeric copolymers  
25 described in WO 95/01383, WO 95/06078, WO 95/06079 and WO  
95/01384, the silicone grafted adhesive polymers disclosed  
in WO 95/04518 or WO 95/05800, the silicone macro-grafted  
copolymers taught in WO 96/21417, the silicone macromers of  
WO 96/32918, the adhesive polymers of WO 98/48770 or WO  
30 98/48771 or WO 98/48772 or WO 98/48776, the graft polymers

of WO 98/51261 and the grafted copolymers described in WO 98/51755.

In certain embodiments of the invention, the styling polymer  
5 is preferably a copolymer having a backbone comprising a  
polyether and, depending from the backbone, a plurality of  
poly (vinyl ester) groups. At least some of the ester  
groups are hydrolysed to the corresponding alcohol,  
preferably at least 50%, more preferably at least 75%, most  
10 preferably at least 95% of the groups are hydrolysed to the  
corresponding alcohol. The poly (vinyl ester) chains  
optionally contain other functional groups in and/or on the  
polymer chain, such as, for example, amide and/or keto  
groups. The copolymer has a polyether backbone which is  
15 obtainable by the polymerisation of one or more alkylene  
oxides. The polyether may comprise a single alkyleneoxy  
group or a mixture of two or more alkyleneoxy groups. The  
polyether may, for example, be based on ethylene oxide,  
propylene oxide, butylene oxide, other alkylene oxides,  
20 polyglycerol and mixtures thereof. Optionally, the backbone  
comprises linkages other than those based on polyether, such  
as, for example, amide or keto linkages. Preferably, the  
copolymer comprises a polyethyleneglycol backbone. The  
copolymer is preferably polyethyleneglycol-co-  
25 polyvinylalcohol having polyvinylalcohol groups bound to the  
polyethyleneglycol i.e., substantially all of the poly (vinyl  
ester) groups are preferably hydrolysed in the copolymers  
used in the compositions of the invention. The copolymer  
can be produced by methods which are well-known to those  
30 skilled in the art. For example, the copolymers are  
obtainable by graft polymerisation. In a method comprising

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graft polymerisation, poly (vinyl ester) groups are preferably grafted onto a polyether and are subsequently hydrolysed to convert at least some of the ester groups to the corresponding alcohol. For example, DE 1 077 430, the contents of which are incorporated herein by reference, describes a process for the preparation of graft polymers of vinyl esters on polyalkylene glycols. The preparation of graft copolymers of polyvinyl alcohol on polyalkylene glycols by hydrolysis of the vinyl esters is described in DE 1 094 457 and DE 1 081 229, both also incorporated herein by reference. The weight average molecular weight of the polyether is preferably from 1 to 100 kDa. Preferred copolymers for use in compositions of the invention have a molar ratio of polyether to total poly(vinyl ester) and polyvinylalcohol groups in the range of from about 95:5 to 5:95, more preferably about 30:70 to about 50:50. Typically, such copolymers have a molar ratio of polyether to total poly(vinyl ester) and polyvinylalcohol groups of about 40:60. The copolymer may be non-cross-linked or cross-linked and it is preferred that the copolymer is cross-linked. Suitable cross-linking agents are those compounds which can bind to two or more polyether, poly (vinyl ester) and/or poly (vinyl alcohol) chains and include, for example, pentaerythritol triallyl ether.

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#### Surfactant

The compositions of the invention may comprise a surfactant in addition to that required for the preparation of any PSA emulsion. The surfactants which are suitable for use in the compositions of the invention may be nonionic, cationic,

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anionic, zwitterionic or a mixture of such surfactants depending on the product form.

The hair styling compositions of the invention preferably  
5 comprise a non-ionic surfactant, in an amount of up to 5%, preferably from 0.01% to 1%, most preferably from 0.02% to 0.8% by weight based on total weight.

Examples of suitable non-ionic surfactants are condensation  
10 products of aliphatic ( $C_8-C_{18}$ ) primary or secondary linear or branched chain alcohols or phenols with alkylene oxides, usually ethylene oxide and generally having at least 15, preferably at least 20, most preferably from 30 to 50 ethylene oxide groups. Other suitable non-ionics include  
15 esters of sorbitol, esters of sorbitan anhydrides, esters of propylene glycol, fatty acid esters of polyethylene glycol, fatty acid esters of polypropylene glycol, ethoxylated esters and polyoxyethylene fatty ether phosphates.

20 Of particular use are those non-ionic surfactants of general formula  $R(EO)_x H$ , where R represents a straight or branched chain alkyl group having an average carbon chain length of 12-18 carbon atoms and x ranges from 30 to 50. Specific examples include steareth-40, steareth-50, cetareth-30,  
25 cetareth-40, cetareth-50 and mixtures thereof. Suitable commercially available examples of these materials include Unicol SA-40 (Universal Preserv-A-Chem), Empilan KM50 (Albright and Wilson), NONION PS-250 (Nippon Oils & Fats), Volpo CS50 (Croda Inc), and Incropol CS-50 (Croda Inc).

### Water

Compositions of the present invention can also include water, preferably distilled or de-ionised, as a carrier for the PSAs, when used in an emulsion form in addition to it being a carrier or a solvent for other components. When present the water will typically be present in amounts ranging from 30% to 98%, preferably from 50% to 95% by weight.

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### Solvent/Carrier

Compositions of the present invention can also include solvents, as a carrier or solvent for the PSAs and other components. When present the solvent will typically be present in amounts ranging from 30% to 98%, preferably from 50% to 95% by weight. Examples of solvents are hydrocarbons, esters, alcohols etc.

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### Hair conditioning agents

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Hair conditioning agents such as hydrocarbons, esters, silicone fluids, and cationic materials may be included in the compositions of the invention. Hair conditioning agents may typically be present in compositions of the invention in amounts of from 0.001% to 10% by weight, preferably 0.1% to 3% by weight. Hair conditioning agents may be single compounds or mixtures of two or more compounds from the same class or different general classes.

25

30 Hair conditioning agents may be included in any of the compositions of the invention, regardless of whether they

contain a hair styling polymer. In one embodiment of the invention, the compositions (such as aerosol mousse formulations, for example) comprise a hair conditioning agent and are substantially free of hair styling polymer.

5

Suitable hydrocarbons can be either straight or branched chain and can contain from about 10 to about 16, preferably from about 12 to about 16 carbon atoms. Examples of suitable hydrocarbons are decane, dodecane, tetradecane, tridecane, and mixtures thereof.

10

Suitable oily or fatty materials are selected from hydrocarbon oils, fatty esters and mixtures thereof.

Straight chain hydrocarbon oils will preferably contain from about 12 to about 30 carbon atoms. Also suitable are polymeric hydrocarbons of alkenyl monomers, such as  $C_2-C_6$  alkenyl monomers.

15

Specific examples of suitable hydrocarbon oils include paraffin oil, mineral oil, saturated and unsaturated dodecane, saturated and unsaturated tridecane, saturated and unsaturated tetradecane, saturated and unsaturated pentadecane, saturated and unsaturated hexadecane, and mixtures thereof. Branched-chain isomers of these compounds, as well as of higher chain length hydrocarbons, can also be used.

20

25



- 21 -

Suitable fatty esters are characterised by having at least 10 carbon atoms, and include esters with hydrocarbyl chains derived from fatty acids or alcohols, Monocarboxylic acid esters include esters of alcohols and/or acids of the formula  $R'COOR$  in which  $R'$  and  $R$  independently denote alkyl or alkenyl radicals and the sum of carbon atoms in  $R'$  and  $R$  is at least 10, preferably at least 20. Di- and trialkyl and alkenyl esters of carboxylic acids can also be used.

10

Particularly preferred fatty esters are mono-, di- and triglycerides, more specifically the mono-, di-, and tri-esters of glycerol and long chain carboxylic acids such as  $C_1$ - $C_{22}$  carboxylic acids. Preferred materials include cocoa butter, palm stearin, sunflower oil, soyabean oil and coconut oil.

Especially preferred is isopropyl myristate.

20 The oily/fatty material is suitably present at a level of from 0.05 to 10, preferably from 0.2 to 5, more preferably from about 0.5 to 3 wt%.

Examples of suitable silicone conditioning agents useful herein can include either cyclic or linear polydimethylsiloxanes, phenyl and alkyl phenyl silicones, and silicone copolyols. Cationic conditioning agents useful  
5 herein can include quaternary ammonium salts or the salts of fatty amines, such as cetyl ammonium chloride, for example.

Compositions according to the invention may, optionally, comprise from 0.1% to 10% by weight of a volatile silicone  
10 as the hair conditioning agent. Volatile silicones are well known in the art and are commercially available and include, for example linear and cyclic compounds. Volatile silicone oils are preferably linear or cyclic polydimethylsiloxanes containing from about three to about nine silicon atoms.

15

The compositions of the invention may optionally comprise a cross-linked silicone polymer.

The cross-linked silicone polymer is preferably a non-rigid  
20 emulsion-polymerised and may be present in compositions of the invention in an amount of up to 10% by weight based on the total weight of the composition, more preferably from 0.2% to 6% by weight, most preferably from 0.5 to 5% by weight.

25

Preferred silicone polymers for use in the invention are polydiorganosiloxanes, preferably derived from suitable combinations of  $R_3SiO_{0.5}$  units and  $R_2SiO$  units where each R independently represents an alkyl, alkenyl (e.g., vinyl),  
30 alkaryl, aralkyl, or aryl (e.g. phenyl) group. R is most preferably methyl.

The preferred silicone polymers of the invention are cross-linked polydimethyl siloxanes (which have the CTFA designation dimethicone), and cross-linked polydimethyl  
5 siloxanes having end groups such as hydroxyl (which have the CTFA designation dimethiconol). Good results have been obtained with cross-linked dimethiconol.

Cross-linking of the silicone polymer is typically  
10 introduced concurrently during emulsion polymerisation of the polymer through the inclusion of the required amount of trifunctional and tetrafunctional silane monomer units, for example, those of formula:

15  $R Si (OH)_3$  wherein R represents an alkyl, alkenyl (e.g. vinyl), alkaryl, aralkyl or aryl (e.g. phenyl) group, preferably methyl.

The degree of cross-linking of the silicone polymer can be  
20 measured as the percentage of branched monomer units in the silicone polymer and is from 0.05% to 10%, preferably being in the range 0.15% to 7%, e.g. from 0.2% to 2%. Increasing cross-linking is found to improve styling benefits but also to reduce conditioning performance somewhat, so compromise  
25 levels must be selected with properties optimised to suit consumer preferences in different cases. Good overall performance has been obtained with dimethiconol 0.3% cross-linked.

30 Suitable emulsion polymerised cross-linked silicone polymers are commercially available or can be readily made using

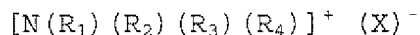
conventional techniques well known to those skilled in the art.

Cross-linked silicone polymers are described in EP 818190,  
5 the contents of which are incorporated herein by reference.

The compositions of the invention may optionally comprise cationic surfactants, used singly or in admixture.

10 Cationic surfactants useful in compositions of the invention contain amino or quaternary ammonium hydrophilic moieties, which are positively charged when, dissolved in the aqueous composition of the present invention.

15 Examples of suitable cationic surfactants are those corresponding to the formula:



20 in which  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  are independently selected from (a) an aliphatic group of from 1 to 22 carbon atoms, or (b) an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to 22 carbon atoms; and X is a salt-forming anion such as those selected from halogen,  
25 (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate nitrate, sulphate, and alkylsulphate radicals.

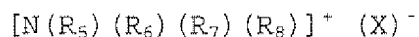
The aliphatic groups can contain, in addition to carbon and  
30 hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those

- 25 -

of about 12 carbons, or higher, can be saturated or unsaturated.

The most preferred cationic surfactants for conditioner  
5 compositions of the present invention are monoalkyl quaternary ammonium compounds in which the alkyl chain length is C8 to C14.

Suitable examples of such materials correspond to the  
10 formula:



in which  $R_5$  is a hydrocarbyl chain having 8 to 14 carbon atoms  
15 or a functionalized hydrocarbyl chain with 8 to 14 carbon atoms and containing ether, ester, amido or amino moieties present as substituents or as linkages in the radical chain, and  $R_6$ ,  $R_7$  and  $R_8$  are independently selected from (a) hydrocarbyl chains of from 1 to about 4 carbon atoms, or (b)  
20 functionalized hydrocarbyl chains having from 1 to about 4 carbon atoms and containing one or more aromatic, ether, ester, amido or amino moieties present as substituents or as linkages in the radical chain, and X is a salt-forming anion such as those selected from halogen, (e.g. chloride,  
25 bromide), acetate, citrate, lactate, glycolate, phosphate nitrate, sulphate, and alkylsulphate radicals.

The functionalised hydrocarbyl chains (b) may suitably contain one or more hydrophilic moieties selected from alkoxy  
30 (preferably  $C_1$ - $C_3$  alkoxy), polyoxyalkylene (preferably  $C_1$ - $C_3$

- 26 -

polyoxyalkylene), alkylamido, hydroxyalkyl, alkylester, and combinations thereof.

Preferably the hydrocarbyl chains  $R_1$  have 12 to 14 carbon atoms, most preferably 12 carbon atoms. They may be derived from source oils which contain substantial amounts of fatty acids having the desired hydrocarbyl chain length. For example, the fatty acids from palm kernel oil or coconut oil can be used as a source of C8 to C12 hydrocarbyl chains.

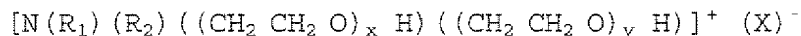
10

Typical monoalkyl quaternary ammonium compounds of the above general formula for use in shampoo compositions of the invention include:

15 (i) lauryl trimethylammonium chloride (available commercially as Arquad C35 ex-Akzo); cocodimethyl benzyl ammonium chloride (available commercially as Arquad DMCB-80 ex-Akzo)

(ii) compounds of the formula:

20



wherein:

25  $x + y$  is an integer from 2 to 20;

$R_1$  is a hydrocarbyl chain having 8 to 14, preferably 12 to 14, most preferably 12 carbon atoms or a functionalised hydrocarbyl chain with 8 to 14, preferably 12 to 14, most  
30 preferably 12 carbon atoms and containing ether, ester, amido

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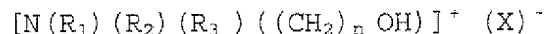
or amino moieties present as substituents or as linkages in the radical chain;

$R_2$  is a  $C_1$ - $C_3$  alkyl group or benzyl group, preferably methyl, and

X is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate nitrate, sulphate, methosulphate and alkylsulphate radicals.

Suitable examples are PEG-n lauryl ammonium chlorides (where n is the PEG chain length), such as PEG-2 cocomonium chloride (available commercially as Ethoquad C12 ex-Akzo Nobel); PEG-2 cocobenzyl ammonium chloride (available commercially as Ethoquad CB/12 ex-Akzo Nobel); PEG-5 cocomonium methosulphate (available commercially as Rewoquat CPEM ex-Rewo); PEG-15 cocomonium chloride (available commercially as Ethoquad C/25 ex-Akzo)

(iii) compounds of the formula:



wherein:

n is an integer from 1 to 4, preferably 2;

$R_1$  is a hydrocarbyl chain having 8 to 14, preferably 12 to 14, most preferably 12 carbon atoms;

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$R_2$  and  $R_3$  are independently selected from  $C_1 - C_3$  alkyl groups, and are preferably methyl, and

$X^-$  is a salt-forming anion such as those selected from  
5 halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate nitrate, sulphate, and alkylsulphate radicals.

Suitable examples are lauryldimethylhydroxyethylammonium  
10 chloride (available commercially as Prapagen HY ex-Clariant)

Mixtures of any of the foregoing cationic surfactants compounds may also be suitable.

15 Examples of suitable cationic surfactants include:

quaternary ammonium chlorides, e.g. alkyltrimethylammonium chlorides wherein the alkyl group has from about 8 to 22 carbon atoms, for example octyltrimethylammonium chloride,  
20 dodecyltrimethylammonium chloride, hexadecyltrimethylammonium chloride, cetyltrimethylammonium chloride, octyldimethylbenzylammonium chloride, decyldimethylbenzylammonium chloride, stearyldimethylbenzylammonium chloride, didodecyldimethylammonium  
25 chloride, dioctadecyldimethylammonium chloride, tallow trimethylammonium chloride, cocotrimethylammonium chloride, and the corresponding salts thereof, e.g., bromides, hydroxides. Cetylpyridinium chloride or salts thereof, e.g., chloride  
30 Quaternium -5  
Quaternium -31



- 29 -

Quaternium -18  
and mixtures thereof.

In the conditioners of the invention, the level of cationic  
5 surfactant is preferably from 0.01 to 10, more preferably  
0.05 to 5, most preferably 0.1 to 2 wt% of the total  
composition.

#### Optional Conditioning Materials

10

Fatty alcohol material

Conditioner compositions of the invention preferably  
additionally comprise a fatty alcohol material. The combined  
15 use of fatty alcohol materials and cationic surfactants in  
conditioning compositions is believed to be especially  
advantageous, because this leads to the formation of a  
lamellar phase, in which the cationic surfactant is  
dispersed.

20

By "fatty alcohol material" is meant a fatty alcohol, an  
alkoxylated fatty alcohol, or a mixture thereof.

Representative fatty alcohols comprise from 8 to 22 carbon  
25 atoms, more preferably 16 to 20. Examples of suitable fatty

#### Product Form

30 Compositions of the present invention are formulated into  
hair styling compositions which may take a variety of forms,

- 30 -

including, for example, mousses, gels, lotions, creams, sprays and tonics. These product forms are well known in the art.

- 5 The preferred product is a spray and/or aerosol and/or mousse.

The compositions of the invention are preferably foaming compositions. Foaming compositions are those compositions  
10 which are capable of forming a foam on dispensation from a suitable container, such as a pressurised aerosol container. More preferably are in the form of an aerosol hair mousse.

Aerosol-form compositions of the invention will include an  
15 aerosol propellant which serves to expel the other materials from the container, and forms the mousse character in mousse compositions. The aerosol propellant included in styling compositions of the present invention can be any liquefiable gas conventionally used for aerosol containers. Examples of  
20 suitable propellants include dimethyl ether and hydrocarbon propellants such as propane, n-butane and iso-butane. The propellants may be used singly or admixed. Water insoluble propellants, especially hydrocarbons, are preferred because they form emulsion droplets on agitation and create suitable  
25 mousse foam densities.

The amount of the propellant used is governed by normal factors well known in the aerosol art. For mousses the level of propellant is generally up to 35%, preferably from  
30 2% to 30%, most preferably from 3% to 15% by weight based on total weight of the composition. If a propellant such as

- 31 -

dimethyl ether includes a vapour pressure suppressant (e.g. trichloroethane or dichloromethane), for weight percentage calculations, the amount of suppressant is included as part of the propellant. For aerosol sprays the levels of  
5 propellant are usually higher; preferably from 30 to 98 wt% of the total composition, more preferably 50 to 95 wt % .

Preferred propellants are selected from propane, n-butane, isobutane, dimethyl ether and mixtures thereof. Preferably,  
10 the propellant comprises dimethyl ether and at least one of propane, n-butane and isobutane.

The method of preparing aerosol hair styling mousse compositions according to the invention follows conventional  
15 aerosol filling procedures. The composition ingredients (not including the propellant) are charged into a suitable pressurisable container which is sealed and then charged with the propellant according to conventional techniques.

20 Compositions of the invention may also take a non-foaming product form, such as a hair styling cream or gel. Such a cream or gel will include a structurant or thickener, typically at a level of from 0.1% to 10%, preferably 0.5% to 3% by weight based on total weight.

25

Examples of suitable structurants or thickeners are polymeric thickeners such as carboxyvinyl polymers. A carboxyvinyl polymer is an interpolymer of a monomeric mixture comprising a monomeric olefinically unsaturated  
30 carboxylic acid, and from about 0.01% to about 10% by weight of the total monomers of a polyether or a polyhydric

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alcohol. Carboxyvinyl polymers are substantially insoluble in liquid, volatile organic hydrocarbons and are dimensionally stable on exposure to air. Suitably the molecular weight of the carboxyvinyl polymer is at least 5 750,000, preferably at least 1,250,000, most preferably at least 3,000,000. Preferred carboxyvinyl polymers are copolymers of acrylic acid cross-linked with allylsucrose or allylpentaerythritol as described in US Patent 2,798,053. These polymers are provided by B.F. Goodrich Company as, for 10 example, CARBOPOL 934, 940, 941 and 980. Other materials that can also be used as structurants or thickeners include those that can impart a gel-like viscosity to the composition, such as water soluble or colloiddally water soluble polymers like cellulose ethers (e.g. 15 methylcellulose, hydroxyethylcellulose, hydroxypropylmethylcellulose and carboxymethylcellulose), guar gum, sodium alginate, gum arabic, xanthan gum, polyvinyl alcohol, polyvinyl pyrrolidone, hydroxypropyl guar gum, starch and starch derivatives, and other thickeners, 20 viscosity modifiers, gelling agents, etc. It is also possible to use inorganic thickeners such as bentonite or laponite clays.

The hair styling compositions of the invention can contain a 25 variety of non-essential, optional components suitable for rendering the compositions more aesthetically acceptable or to aid use, including discharge from the container, of the product. Such conventional optional ingredients are well known to those skilled in the art, e.g. preservatives such 30 as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea, fatty alcohols such as cetearyl

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alcohol, cetyl alcohol and stearyl alcohol, pH adjusting agents such as citric acid, succinic acid, sodium hydroxide and triethanolamine, colouring agents such as any of the FD&C or D&C dyes, perfume oils, chelating agents such as  
5 ethylenediamine tetraacetic acid, and polymer plasticising agents such as glycerin and propylene glycol

The invention will now be further illustrated by the following, non-limiting Examples.

10

Examples of the invention are illustrated by a number, comparative examples are illustrated by a letter.

The following PSA emulsions were used:

15

The PSA emulsions are defined below:

Product code	DC® 5-7300 18393-45	DC® 5-7200 17724-65-A	DC® 5-7200 17724-65-B	DC® 5-7200 17724-65-C
% internal phase(solvent + PSA)	60	60	60	60
PSA:solvent ratio	40:60	60:40	60:40	60:40
Solvent	isododecane	1 cst PDMS	1 cst PDMS	1 cst PDMS
Resin:Polymer ratio	65:35	65:35	65:35	55:45
Particle size D50 (Microtrack)	4.312µm	10µm	4µm	14µm
Emulsifier	anionic	anionic	anionic	anionic

## Aerosol Mousse Example 1

Ingredient	Trade Name	Raw Material Supplier	%wt. raw material
PSA emulsion	DC® 5-7200 17724-65-A	DOW CORNING	2.8
Cetearyl alcohol	LAUREX CS	ALBRIGHT & WILSON	0.64
Behenyl trimethyl ammonium chloride	GENAMIN KDMP	CLARIANT	0.32
Isopropyl myristate	ISOPROPYL MYRISTATE	UNIQEMA	2
Polyoxyethylene (10) lauryl ether	EMALEX 710	NIHON EMULSION CO., LTD	1
Propane/Butane gas	CAP 40	CALOR GAS	8
Water	DEIONISED WATER	Local supply	Up to 100

## Aerosol mousse Example 2

Ingredient	Trade Name	Raw Material Supplier	%wt. raw material
PSA emulsion	DC® 5-7200 17724-65-B	DOW CORNING	2.8
Cross-linked methylpolysiloxane	DOW CORNING 2-1787 HVF EMULSION	DOW CORNING	2.8
Methylpolysiloxane emulsion (1MMcs)	DOW CORNING 2-1784 HVF EMULSION	DOW CORNING	2
Polyoxyethylene (10) lauryl ether	EMALEX 710	NIHON EMULSION CO., LTD	1
Dimethyl ether	DYMEL A	DUPONT	2
Propane/Butane gas	CAP 40	CALOR GAS	6
Water	DEIONISED WATER	Local supply	Up to 100



## Cream / Lotion Example 3

Ingredient	Trade Name	Raw Material Supplier	%wt. raw material
PSA emulsion <sup>1</sup>	DC® 5-7200 17724-65-C	DOW CORNING	2.8
Cetearyl alcohol	LAUREX CS	ALBRIGHT & WILSON	0.64
Behenyl trimethyl ammonium chloride	GENAMIN KDMP	CLARIANT	0.32
Isopropyl myristate	ISOPROPYL MYRISTATE	UNIQEMA	2
Cationic acrylic homopolymer dispersed in an emollient ester	SALCARE SC96	ALLIED COLLOIDS	1.2

Feel performance

5 The test

18 trained panellists used the both prototype formulations  
and a control in duplicate for three days each in their  
10 homes and have scored the products using a 100 point scale  
on a number of attributes including stickiness of hair and  
stickiness of hand.

15

					4	A
Ingredient	Trade Name	Raw Material Supplier	%wt. active ingredient	%wt. active ingredient		
DC® 5-7200 17724-65-B	-	DOW CORNING	1.7			
Copolymer of 3-methyl-1-vinyl-1H-imidazolium chloride and 1-vinyl-2pyrrolidone (50:50)	Luviquat* FC550	BASF PLC		2		
Cetearyl alcohol	LAUREX CS	ALBRIGHT & WILSON	0.6	0.6		
Behenyl trimethyl ammonium chloride	GENAMIN KDMP	CLARIANT	0.3	0.3		
Isopropyl myristate	ISOPROPYL MYRISTATE	UNIQEMA	2	2		
Polyoxyethylene (10) lauryl ether	EMALEX 710	NIHON EMULSION CO., LTD	1	1		
Propane/Butane gas	CAP 40	CALOR GAS	8	8		
Water	DEIONISED WATER	Local supply	Up to 100	Up to 100		

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Test protocol details

The panellists typically apply 5g of product to their hair. They typically wash their hair every night and apply the mousse to their hair the following morning following their usual styling routine. The panellists used each product for 3 consecutive days and scored it on the third day using the score-sheet provided. Once all mousses have been evaluated in the order set out the test is completed.

10

Results

	Normalised average scores* (%)	
	4	A
Stickiness of hand	-9	16
Stickiness of hair	3	9
Volume down	8	6

15

Example 4 gives similar volume control to comparative Example A, but it is perceived as less sticky on hair and much less sticky on hands.

20

Styling performance

The styling performance of two PSA emulsions was compared to that of Luviquat\* FC550 a conventional styling polymer.

25

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A set of 5 2g/25cm switches made from 'virgin' Spanish hair was washed with 16% wt. SLES.2EO. 1 ml solution was applied along the length of the hair and agitated for 30 sec. The switches were then rinsed with warm water for 30 sec.

5 Further 1 ml surfactant solution was applied and the hair was agitated for 30 sec again followed by 1 min rinse with warm water.

The towel dried hair was then treated with the Examples  
10 exemplified below:

			% active ingredient		
			B	5	6
Copolymer of 3-methyl-1-vinyl-1H-imidazolium chloride and 1-vinyl-2pyrrolidone (50:50)	Luviquat* FC550	BASF PLC	1.2		
PSA emulsion	DC® 5-7200 17724-65-A	DOW CORNING		1.2	
PSA emulsion	DC® 5-7300 18393-45	CALOR GAS			1.2
Polyoxyethylene (10) lauryl ether	EMALEX 710	NIHON EMULSION CO., LTD	1	1	1
Propane/Butane gas	CAP40	CAP 40	8	8	8
Water		LOCAL SUPPLY	Up to 100	Up to 100	Up to 100

1g of mousse was applied to each set of 5 2g/25cm hair switches ensuring even distribution. Each switch was wound  
15 on a pegboard. The pegboards were then placed in a drying

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cabinet @ 65°C/10% RH for 3h. Prior removing the curls, the  
 pegboards were left at ambient conditions for 30 min. The  
 curls were then hung on a panel and placed in humidity  
 chamber at 30°C/90%RH. The curls were photographed every 5  
 5 min and a record of the curl length was kept.

The generated colour digital images were rendered into grey-  
 scale format. The grey-scale images were subsequently  
 converted into a binary form (i.e. composed only of black  
 10 and white pixels). The dimensionless 2D projection area of  
 each switch was used as a measure for the extent of switch  
 spread out (i.e. loss of curliness). The projection area  
 was calculated from the number of black pixels. The data  
 were normalised by taking the ratio of the projection area  
 15 to the average switch projection area calculated for the set  
 of switches treated with Example 6.

	B	5	6	water
Normalised projection area after 1h @ 30°C/90%RH	1.34 ± 0.13	1.27 ± 0.13	1	2.2 ± 0.13

The pressure sensitive adhesives give similar or better curl  
 20 retention to that of the styling polymer.

The styling performance of pressure sensitive adhesive  
 emulsion was tested against conventional conditioning  
 silicone and x-linked silicone used in styling formulations.

			% active ingredient		
			7	C	D
PSA emulsion	DC® 5-7200 17724-65-A	DOW CORNING	1.2		
Methylpolysiloxane emulsion (1MMcs)	DOW CORNING 2- 1784 HVF EMULSION	DOW CORNING		1.2	
Cross-linked methylpolysiloxane	DOW CORNING 2- 1787 HVF EMULSION	DOW CORNING			1.2
Polyoxyethylene (10) lauryl ether	EMALEX 710	NIHON EMULSION CO., LTD	1	1	1
Propane/Butane gas	CAP40	CAP 40	8	8	8
Water		LOCAL SUPPLY	Up to 100	Up to 100	Up to 100

- 5 Three sets of 5 2g/25cm 'virgin' Spanish hair were washed and treated with formulations 7, C and D as described above. The switches were then hung vertically and left to dry @ 20°C/50%RH. The dried switches were photographed and the obtained images were analysed in the manner described above
- 10 to obtain the average normalised projection area, which was used as a measure of the extent of switch expansion. Example 7 was used for control.

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	7	C	D
Normalised projection area	1	$1.8 \pm 0.1$	$3.6 \pm 0.4$

The pressure sensitive adhesive gives much lower hair volume than the conditioning and the styling silicone.



CLAIMS

1. A mousse, cream, lotion or spray leave on hair treatment  
5 composition, comprising a silicone pressure sensitive  
adhesive wherein the pressure sensitive adhesive is in  
the form of an emulsion.
2. A hair treatment composition according to claim 1 which  
10 further comprises a propellant.
3. A hair treatment composition according to claim 1 or  
claim 2 in which the propellant is a hydrocarbon gas.
- 15 4. A hair treatment composition according to any preceding  
claim further comprising a hair conditioning agent.
5. A composition according to any preceding claim, wherein  
the emulsion comprises a disperse solvent phase in a  
20 continuous water phase in the presence of a surfactant.
6. A composition according to claim 5, wherein the solvent  
has a boiling point below 300°C.
- 25 7. A composition according to claim 5 or claim 6, wherein  
the solvent comprises silicone.
8. A composition according to claim 5, wherein the  
dispersed solvent phase comprises 20 to 80 % by weight  
30 of the silicone pressure sensitive adhesive.

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9. A composition according to claim 8 wherein the pressure  
sensitive adhesive comprises a) from 40 to 70 parts by  
weight of at least one silicone copolymer resin; and  
b) 30 to 60 parts by weight of at least one  
5 polydiorganosiloxane.

10. A method for styling hair which comprises contacting  
the hair with a composition in accordance with any  
preceding claim.

10

11. The use of silicone PSA's in a hair treatment  
composition to impart hair styling without stickiness.

15

ABSTRACT

A mousse, cream, lotion or spray leave on hair treatment  
5 composition comprising a silicone pressure sensitive  
adhesive.

